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EVALUATION OF ACTIVATED CARBON FOR ENHANCED COD REMOVAL FROM PHARMACEUTICAL WASTEWATER

VOLUME I. FINAL REPORT

by

Richard Osantowski and Richard Wullschleger
Rexnord Inc.
Milwaukee, Wisconsin 53214

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Project Officer

Clyde R. Dempsey
Industrial Wastes and Toxics Technology Division
Water Engineering Research Laboratory
Cincinnati, Ohio 45268

WATER ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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16. ABSTRACT

From September to December, 1984 pharmaceutical plant wastewater containing high concentrations of total chemical oxygen demand (TCOD) in the raw waste and treated effluent was treated in trailer mounted pilot plants. The biological treatment train used to treat raw wastewater consisted of three activated sludge systems operated in parallel. Powdered activated carbon (PAC) was added to two of the units in selected dosages. The third unit was used as a control. The physical-chemical treatment train studied in the treatment of pharmaceutical plant effluent consisted of chemical coagulation with alum and anionic polymer; pH adjustment with caustic (when needed); clarification; multi-media filtration and granular activated carbon (GAC) adsorption.

The PAC enhanced biological treatment train as operated during the test period reduced influent TCOD concentration to well below the plant best practicable control technology currently available (BPT) TCOD level. PAC also improved the settling rate of the mixed liquor suspended solids when compared to the control. A viscous floating mass of mixed liquor solids (VFMLS) developed in the PAC units and resulted in premature termination of the study. The VFMLS did not appear in the control. The GAC physical-chemical treatment train was also capable of reducing pharmaceutical plant effluent TCOD levels to below the average BPT level.

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Wastewater	Activated Sludge	Stationary Sources	
Pharmaceutical	Activated Carbon	Biological Oxidation	
Chemical Oxygen Demand	Organic Compounds	Physical-Chemical Treatment	
Clarification	Powdered Carbon		

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FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air and water systems. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act and the Toxic Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the research and the user community.

This report details the results of an in-depth pilot plant study to evaluate enhanced chemical oxygen demand removal from pharmaceutical wastewater by the use of activated carbon. Both physical-chemical and biological treatment technologies were studied. Volume I discusses the project and analyzes, interprets and summarizes the results. Volume II contains the appendices which includes all of the data and additional supporting information.

Francis T. Mayo, Director
Water Engineering Research Laboratory

ABSTRACT

In November, 1982 the EPA proposed effluent limitations and standards (EPA 440/1-82/084) for the pharmaceutical manufacturing point source category. Some of the proposed regulations limited the discharge of the nonconventional pollutant, total chemical oxygen demand, (TCOD), from existing and new source fermentation (A) and chemical synthesis (C) pharmaceutical manufacturing facilities. However, due to a lack of information on applicable TCOD removal technologies, limitations and standards for TCOD were not promulgated along with the other regulations for A and C Plants on October 27, 1983.

In April, 1984, EPA decided to conduct pilot scale performance evaluations of activated carbon treatment technologies utilizing actual pharmaceutical wastewaters. The purpose of these studies was to help evaluate the ability of these technologies to consistently achieve reductions in the effluent TCOD of pharmaceutical wastewater from fermentation and chemical synthesis wastewaters.

Technologies that were selected for evaluation included:

(1) powdered activated carbon (PAC) addition to an activated sludge system (PACT ®); and

(2) granular activated carbon treatment of pharmaceutical plant secondary effluent.

From September to December, 1984 pharmaceutical plant wastewater containing high concentrations of TCOD in the raw waste and treated effluent was treated in trailer mounted pilot plants. The biological treatment train consisted of three activated sludge systems operated in parallel. Powdered activated carbon was added to two of the units in selected dosages. The third unit was used as a control. The physical-chemical treatment train consisted of chemical coagulation with alum and anionic polymer; pH adjustment with caustic (when needed); clarification; multi-media filtration and granular activated carbon (GAC) adsorption.

The PAC enhanced biological treatment train as operated during the test period reduced influent TCOD concentration to well below the plant best practicable control technology currently available (BPT) TCOD level. PAC also improved the settling rate of the mixed liquor suspended solids when compared to the control unit. A viscous floating mass of mixed liquor solids (VFMLS) developed in the PAC units near the end of Phase IV of the study and resulted in premature termination of the study. The VFMLS did not appear in the control. The GAC physical-chemical treatment train was also capable of reducing pharmaceutical plant effluent TCOD levels to below the average BPT level.

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LIST OF ABBREVIATIONS AND CONVERSIONS

ABBREVIATIONS

ACA -- activated carbon adsorption

BAT -- best available technology economically achievable

BPT -- best practicable control technology currently available

BTS-1 -- Biological Treatment System - 1

BTS-2 -- Biological Treatment System - 2

BTS-3 -- Biological Treatment System - 3

°C -- degrees Centigrade

Cl -- chlorides

CLASS -- chemical laboratory analysis scheduling system

cm -- centimeter

DMACT -- Dynamic Minicolumn Adsorption Technique

DO -- dissolved oxygen

EBCT -- empty bed contact time

ESE -- Environmental Science and Engineering

ft -- foot (feet)

F/M -- food to micro-organism ratio

g -- gram

GC -- gas chromatography

GC/FID -- gas chromatography/flame ionization detection

GC/FTIR -- gas chromatography/Fourier transform infrared

GC/MS -- gas chromatography/mass spectrometry

GAC -- granular activated carbon

gal -- gallon

gpm -- gallons per minute

HP -- horsepower

HPLC/MS -- high pressure liquid chromatography/mass spectrometry

HRT -- hydraulic retention time
in -- inch
kg -- kilograms
KW -- kilowatt
L -- liter
lb -- pound
m -- meter
m/e -- ratio of mass to charge
mg -- milligram
mgd -- million gallons per day
mg/L -- milligrams per liter
min -- minute
ml -- milliliter
ML -- mixed liquor
MLSS -- mixed liquor suspended solids
MLVSS -- mixed liquor volatile suspended solids
MWTS #1 -- Mobile Wastewater Treatment System # 1
MWTS #3 -- Mobile Wastewater Treatment System # 3
n -- number of observations
NH_3 -- ammonia
NIBOD -- nitrogen inhibited biochemical oxygen demand
NISBOD -- nitrogen inhibited soluble biochemical oxygen demand
NO_2 -- nitrite
NO_3 -- nitrate
NSPS -- new source performance standards
PAC -- powdered activated carbon
P727 -- Percol 727 polymer
P728 -- Percol 728 polymer
P757 -- Percol 757 polymer
P763 -- Percol 763 polymer
POI -- point of interface
psi -- pounds per square inch
psig -- pounds per square inch gauge
QA -- quality assurance

QC -- quality control
RAS -- return activated sludge
RS -- return sludge
RPM -- revolutions per minute
SBOD -- soluble biochemical oxygen demand
SCOD -- soluble chemical oxygen demand
sec -- second
SRT -- solids retention time
STOC -- soluble total organic carbon
SVI -- sludge volume index
TBOD -- total biochemical oxygen demand
TCOD -- total chemical oxygen demand
TKN -- total Kjeldahl nitrogen
TOC -- total organic carbon
TP -- total phosphate
TSS -- total suspended solids
ul -- microliter
VFMLS -- viscous floating m[illegible] liquor solids
VSS -- volatile suspended solids

CONVERSIONS

$^{o}F = 1.8^{o}C + 32$
ft x 30.48 = cm
gal x 3.785 = l
gal x $3.785 \times 10^{-3} = m^3$
gpd/ft^2 x 0.04 = m^3/day-m^2
gpm x 3.785 = l/min
gpm/ft^2 x 40.74 = l/min-m^2
HP x 7.5 = KW
in x 2.54 = cm
lb x 0.454 = kg
psi x 703.1 = kg/m^2

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Special thanks are also extended to Mr. Dempsey and Mr. Glenn Shaul of the EPA Water Engineering Research Laboratory for their assistance in field operation of the biological and physical/chemical pilot plants.

The assistance provided by the Rexnord Environmental Product Development Division is also acknowledged. Under the direction of Mr. Charles Applegate, a computer program format was developed and used as the basis for the graphics and statistics used to discuss the report results. This work was offered to the project entirely through an in-kind contribution.

Laboratory support was provided throughout the study by Environmental Science and Engineering, Inc. (ESE), Gainesville, Florida. The assistance provided by Ms. Margaret Farrell, Dr. David Powell and Mr. Hugh Prentice was particularly helpful. ESE was also the major author on Sections 7 and 10 of the report and provided analysis of the floating mixed liquor suspended solids discussed in Section 8.

SECTION 1

INTRODUCTION

The pharmaceutical manufacturing point source category manufactures biological products, medicinal chemicals, botanical products and pharmaceutical products covered by Standard Industrial Classification Code Numbers 2831, 2833 and 2834, as well as other commodities.

The industry is characterized by diversity of product, process, plant size and process stream complexity. In developing the effluent limitations for this category as required by the Clean Water Act and related settlement agreements, subcategories based on process characteristics were defined for purposes of technical evaluation and were later found to be appropriate for regulation. These subcategories are:

Subcategory A - Fermentation Products
Subcategory B - Biological and Natural Extraction Products
Subcategory C - Chemical Synthesis Products
Subcategory D - Formulation Products
Subcategory E - Pharmaceutical Research

On November 17, 1976, the U.S. Environmental Protection Agency (EPA) promulgated interim final best practicable control technology currently available (BPT) regulations for the pharmaceutical manufacturing point source category. Among other things, monthly limitations based on percent removal were set at 74% for total chemical oxygen demand (TCOD). No daily maximum was established. The technical basis for these regulations is provided in "Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Pharmaceutical Manufacturing Point Source Category," December 1976 (EPA 440/1-75/060) (1).

However, raw wastewaters from Subcategories A and C are characterized by high TCOD concentrations (up to 10,000 mg/L and above). Consequently, plants can meet BPT while discharging effluents having high TCOD levels.

On November 26, 1982, the EPA proposed best available technology economically achievable (BAT) and new source performance standards (NSPS) designed to control the discharge of the nonconventional pollutant, TCOD, from pharmaceutical manufacturing facilities. The proposed limitations were:

Regulation	Maximum 30-Day Average (mg/L)	Daily Maximum (mg/L)
BAT	570	1024
NSPS	449	853

The technical basis for these proposed regulations are provided in "Proposed Development Document for Effluent Limitations Guidelines and Standards for the Pharmaceutical Point Source Category," November 1982 (EPA 440/1-82/084) (2). Subsequent to the proposal and in response to comments, the Agency decided to return to the 1976 BPT subcategorization scheme. As a result, the proposed TCOD limitations and standards quoted above are no longer appropriate for comparison. A more appropriate comparision level is the specific BPT TCOD level required (3).

Industry also commented that the technology basis supporting the proposed TCOD limitations was inadequate and that the Agency had not indicated what chemical pollutants it was attempting to control through the TCOD limitations.

On October 27, 1983, the EPA promulgated final Pharmaceutical Manufacturing Point Source Category Effluent Limitations Guidelines, Pretreatment Standards and New Source Performance Standards(3). However, a final decision on appropriate BAT limitations and NSPS for the nonconventional pollutant TCOD was postponed until additional information was obtained on the identity of the pollutants that contribute to the TCOD and on applicable removal technologies.

By way of responding to these additional information needs, the Effluent Guidelines Division (now the Industrial Technology Division - ITD) of EPA initiated a work/study program designed to:

1. Determine the constituents of the high TCOD concentrations in biologically treated effluents of pharmaceutical manufacturing plants.

2. Evaluate the ability of activated carbon adsorption (ACA) technologies to reduce the effluent TCOD levels.

An important part of Objective #2 involved demonstrating through pilot plant studies, the capability of ACA technology to reduce pharmaceutical plant effluent TCOD levels. On April 27, 1984, the ITD requested assistance from the Water Engineering Research Laboratory, Cincinnati in conducting the necessary pilot plant evaluations.

Two technologies were evaluated at a Subcategory A and C pharmaceutical manufacturing plant which employed secondary treatment and reported high TCOD levels in their discharge monitoring report. The two technologies were:

1. Powdered Activated Carbon (PAC) addition to the activated-sludge aeration basin for the treatment of raw wastewater.

2. Granular Activated Carbon (GAC) treatment of the secondary effluent.

This study was conducted at a pharmaceutical plant from September 1 to December 7, 1984. The pilot testing activity was performed by the EnviroEnergy Technology Center of Rexnord, Milwaukee, Wisconsin. Analytical support throughout the project was provided by Environmental Science and Engineering of Gainesville, Florida.

SECTION 2

CONCLUSIONS

The purpose of this study was to evaluate the effectiveness of selected biological and physical-chemical treatment technologies for reducing contaminants present in a pharmaceutical wastewater. TCOD was the parameter selected to measure the effectiveness of treatment.

BIOLOGICAL STUDY CONCLUSIONS

1. Both the full-scale biological treatment plant and the pilot scale control plant exceeded the BPT minimum average monthly TCOD removal of 74 percent. TCOD removals were 80 percent and 84 percent for the full-scale and pilot control plant, respectively, for the entire test period.

2. Effluent soluble COD (SCOD) concentrations were significantly reduced by the addition of powdered activated carbon (PAC) to the feed to activated sludge treatment. Effluent SCOD concentrations were reduced by 44 percent, 54 percent, 68 percent and 67 percent of the control plant effluent SCOD concentrations when adding 208 mg/L, 496 mg/L, 827 mg/L and 1520 mg/L PAC, respectively.

3. The addition of PAC resulted in a very small improvement in the mixed liquor suspended solids (MLSS) settling rate in spite of the higher total suspended solids (TSS) in the mixed liquor containing PAC. The MLSS settling rate remained at very low levels, however, ranging from 0.01 to 0.05 cm/min. Treatment of the MLSS with an organic polyelectrolyte improved settling rates markedly.

4. Effluent TSS optimization was not an objective of this study. However, the data indicated that PAC addition did not have a significant impact on the effluent TSS.

5. Denitrification developed in the final clarifier of both units containing PAC, causing some solids to float. Denitrification was not apparent in the control unit.

6. A viscous floating mass of mixed liquor solids (VFMLS) developed in both PAC units near the end of Phase IV and resulted in premature termination of the study. The VFMLS was very cohesive and difficult to re-disperse in water. The VFMLS did not appear in the control unit during these tests.

7. The PAC/activated sludge process cannot be recommended as a viable process for this plant's wastewater until the cause of the viscous floating MLSS is identified and adequate safeguards against its occurrence are demonstrated.

8. Type 021N and H. hydrossis organisms were found in "abundant" or "excessive" amounts in both units containing PAC. H. hydrossis was also "abundant" in the control unit but only a "few" Type 021N organisms were present. For each pilot unit, the distribution of organisms was similar for mixed liquor samples and VFMLS samples.

PHYSICAL-CHEMICAL TREATMENT STUDY CONCLUSIONS

The results of the pilot program demonstrated that the physical-chemical technology investigated was effective in reducing pharmaceutical plant secondary effluent contaminants as measured by TCOD and SCOD to low levels. Physical-chemical treatment technologies studied included chemical treatment/clarification, multi-media filtration and granular activated carbon. Principal conclusions from the physical-chemical pilot research study are summarized below.

Chemical Clarification

1. Clarification removed an average of 43 percent of the influent suspended solids and 44 percent of the total biochemical oxygen demand (TBOD) from full-scale plant secondary effluent. Similarly, TCOD was reduced by an average of 28 percent. Required alum and polymer dosages ranged from 200 to 1340 mg/L and 0.2 to 3.0 mg/L, respectively.

2. At the plant studied, pretreatment of the secondary effluent for TSS removal was necessary; however optimizing this pretreatment was not an objective of this study. Because of the rapidly changing chemical demand of the pilot plant feed water, it was often difficult to maintain consistent TSS removal. Chemical dosages were adjusted routinely using on-site jar tests as a basis for change.

3. About 0.8 m^3 (200 gal) of sludge were produced for every 3.8 m^3 (1000 gal) of wastewater treated based on 30 minute settling tests.

Multi-media Filtration

1. A design flaw in the multi-media filter prevented proper bed stratification following backwash. As a result, the filtration data collected were considered not representative and were not evaluated.

Activated Carbon

1. GAC was technically effective in reducing pharmaceutical plant activated sludge effluent SCOD concentration.

2. The combination of biological treatment and GAC reduced the influent TCOD from 7060 mg/L to an average effluent SCOD of from 200 to 400 mg/L.

3. Carbon usage was found to be a function of the effluent SCOD concentration and the empty bed contact time (EBCT). A summary of the carbon usage rates determined from the pilot study are shown below.

Carbon Usage, kg/1000 L

	Design effluent SCOD, mg/L		
EBCT, min	300	400	500
35	3.1	2.6	1.9
70	2.1	2.1	1.9
105	2.8	2.1	1.5
140	2.1	1.7	1.2

4. Samples of carbon column influent and effluent were collected for suspended solids although TSS removal was not a primary objective. Based on composite sample results, the TSS removal for Run No. 1 (downflow mode) was 59 percent. The Run No. 2 TSS removal efficiency was 14 percent for upflow operation.

5. TBOD removal for Run No. 1 was 52 percent compared to 30 percent for Run No. 2.

6. The compound 2-butyl-4-amino-5-pyrimidyl-carbinol was tentatively identified as being present in the biologically treated effluent from the pilot plant control unit at a concentration of approximately 4 mg/L and dimethylphenol was tentatively identified as a minor component in this wastewater but at a much lower concentration.

7. The removal of the two tentatively identified specific organic compounds (2-butyl-4-amino-5-pyrimidyl-carbinol and dimethylphenol) and many unidentified specific organics as measured by gas chromatography is related to the removal of SCOD by GAC treatment. The decrease in SCOD after carbon treatment was much less than the reduction of the area under the gas chromatogram peaks.

SECTION 3

RECOMMENDATIONS

BIOLOGICAL TREATMENT

Operational problems were encountered with the pilot units during this study and a significant VFMLS problem was encountered in the later stages of Phase IV in the PAC systems.

1. It is recommended that a major study be performed to determine the cause of the VFMLS problems and to optimize biological control. In addition, it is believed that these operational problems can be minimized by changes in operating conditions.

2. It is recommended that further pilot plant testing be performed using:

    a. A single, completely mixed aeration tank for each pilot unit. This will more closely simulate full-scale plant operation and eliminate problems in distribution of air to the several aeration tank cells. Adequate air supply should be available for all pilot units.

    b. The provision for adequate nutrients at all times.

    c. The addition of polyelectrolyte to the mixed liquor prior to the clarifiers to improve effluent clarity and MLSS settling rates.

    d. Provision for frequent, automatic agitation of the settled sludge in the pilot plant clarifiers to prevent bridging of solids in the clarifier bottom. With improved MLSS settling rates and prevention of bridging of clarifier sludge solids, it is expected that the MLSS can be returned to aeration more quickly and reduce the tendency for denitrification in the PAC pilot plant clarifiers.

    e. Evaluate better hydraulic and solids retention times to eliminate/minimize sludge bulking.

PHYSICAL-CHEMICAL TREATMENT

GAC was technically effective in reducing pharmaceutical plant effluent SCOD concentrations.

The pilot study determined that proper pretreatment of the wastewater for maximum suspended solids (and corresponding TCOD) removal is an important consideration. Due to the variability in the secondary effluent, operational problems were encountered primarily related to TSS removal (although this was not a major project objective). The following operational problems should be addressed:

1. It is recommended that flotation be evaluated as an alternate to gravity settling clarification for removal of suspended solids in the pharmaceutical plant effluent.

2. Additional studies should be performed to identify chemicals that could consistently produce good settling of the pharmaceutical plant effluent TSS.

3. It is recommended that additional multi-media filtration studies be conducted with a properly designed and operated pilot plant filter.

4. Studies should be conducted to determine the dewaterability of sludge produced from clarification of the pharmaceutical plant effluent.

SECTION 4

DESCRIPTION OF THE RESEARCH SITE

GENERAL

The pilot plant work on enhanced treatment of pharmaceutical wastewater was performed at a Subcategory A (fermentation products) and C (chemical synthesis products) pharmaceutical plant which has an average employment of about 400 people.

PLANT LAYOUT/WASTEWATER FEED SOURCES

Process wastewater and sanitary wastewater from this plant are treated biologically. A diagram of the treatment system is shown on Figure 1. The process wastewater flows through an equalization basin and a pH-neutralization tank prior to being mixed with a nominal amount (<6%) of macerated, chlorinated sanitary wastewater. The combined flow is then pumped to an activated sludge treatment system consisting of aeration basins and two intermediate clarifiers.

Following separation of the mixed liquor in the clarifiers, the effluent is then pumped to trickling filters for further treatment. The last unit operation in the wastewater treatment train is final clarification. The treated effluent is then discharged to a river.

The feed source to the biological pilot plants was raw, equalized, neutralized, pharmaceutical plant wastewater. The feed source to the physical-chemical pilot plants was biologically treated and clarified pharmaceutical wastewater. This water was pumped from the secondary clarifier effluent as illustrated on Figure 1, from September 5-17, 1984. After a brief period of pilot testing, it became evident that this waste stream contained a large amount of suspended solids which were not easily settled in the pilot scale clarifier. Since the primary objective of the physical-chemical program was to evaluate the ability of granular activated carbon to remove soluble organics as opposed to TSS removal (which was not an objective) from the treated pharmaceutical plant wastewater, it was decided to relocate the pilot plant feed source to the final clarifier effluent trough. The water at this point was quite consistent with regard to suspended matter and had essentially the same concentration of SCOD as the secondary clarifier effluent. Thus, for the duration of the project (9/17 - 12/4), the final clarifier effluent was used as the pilot plant feedwater for the physical-chemical system.

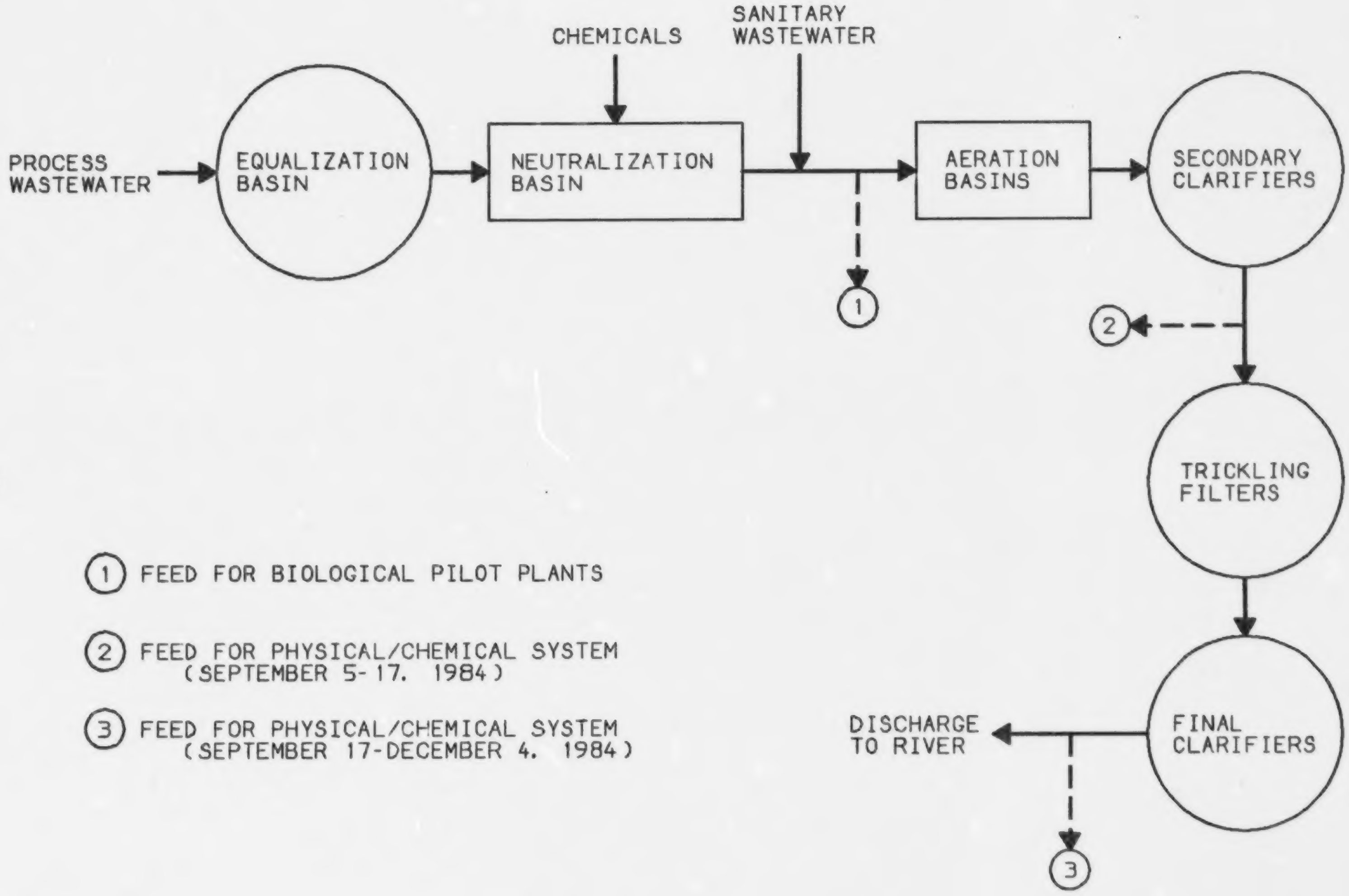

PROCESS WASTEWATER
EQUALIZATION BASIN
CHEMICALS
NEUTRALIZATION BASIN
SANITARY WASTEWATER
AERATION BASINS
SECONDARY CLARIFIERS
TRICKLING FILTERS
FINAL CLARIFIERS
DISCHARGE TO RIVER
①
②
③
① FEED FOR BIOLOGICAL PILOT PLANTS
② FEED FOR PHYSICAL/CHEMICAL SYSTEM (SEPTEMBER 5-17. 1984)
③ FEED FOR PHYSICAL/CHEMICAL SYSTEM (SEPTEMBER 17-DECEMBER 4. 1984)

Figure 1. Schematic Flow Diagram of Full-Scale Treatment Plant.

Reproduced from best available copy.

SECTION 5

DESCRIPTION OF THE PILOT EQUIPMENT

INTRODUCTION

This section describes the pilot scale equipment used at the pharmaceutical plant research site. All of the treatment technologies investigated were located either on the EPA Mobile Wastewater Treatment Systems (MWTS #1 and #3) or in an adjacent support trailer. In addition, a mobile testing laboratory was used for on-site analysis.

The trailer arrangement is shown on Figure 2 with the mobile lab in the right foreground. The support trailer housing additional laboratory equipment, automatic samplers and a third biological treatment system is shown in the left hand side of the figure. In the right background of Figure 2 can be seen MWTS #1 and MWTS #3 (extreme rear). The physical-chemical pilot plant equipment was located in MWTS #1 and the activated sludge pilot reactors were housed in MWTS #3.

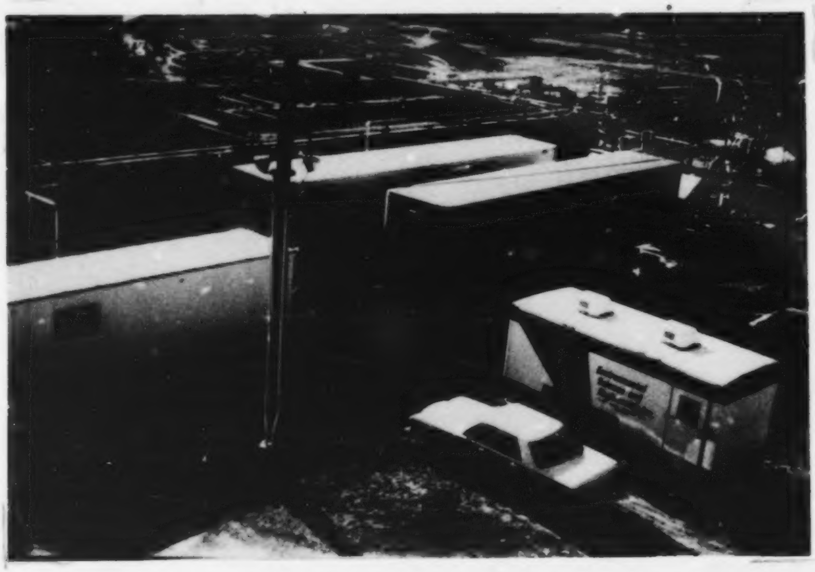


Figure 2. Trailer Arrangement.

DESCRIPTION OF THE BIOLOGICAL PILOT PLANTS

The pilot biological treatment study was performed using the two biological units, Biological Treatment System-1 (BTS-1) and Biological Treatment System-2 (BTS-2), in MWTS #3 as illustrated on Figure 3 and a smaller EPA biological pilot plant, Biological Treatment System-3 (BTS-3), shown on Figure 4.

The two activated sludge treatment systems located in the MWTS #3 were used as the experimental units. Each system consisted of an aeration tank, 5940 liters (1570 gal) in BTS-1 and 5560 liters (1470 gal) in BTS-2, and a 2840 liter (750 gal) circular, center feed, clarifier. Each aeration tank had three aeration cells in series. The air flow to each cell could be controlled independently. Pumps required to supply wastewater, return sludge and add chemicals were available for each system. Chemical feeders were used to pump a PAC slurry and sodium hydroxide which was used on an as needed basis to maintain the pH in an acceptable range. For this project, different dosages of powdered activated carbon were added to the first aeration cell of each experimental unit. Additional information on the pilot scale biological experimental units is presented in Appendix A.

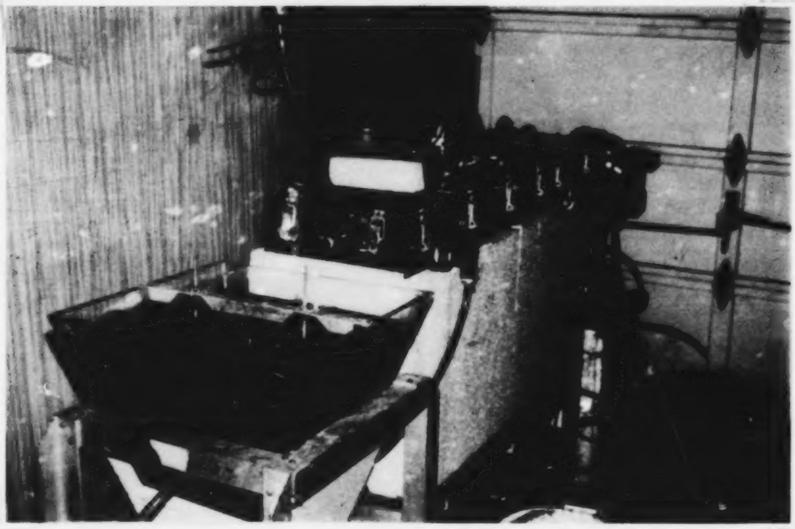


Figure 4. Biological Treatment System - 3.

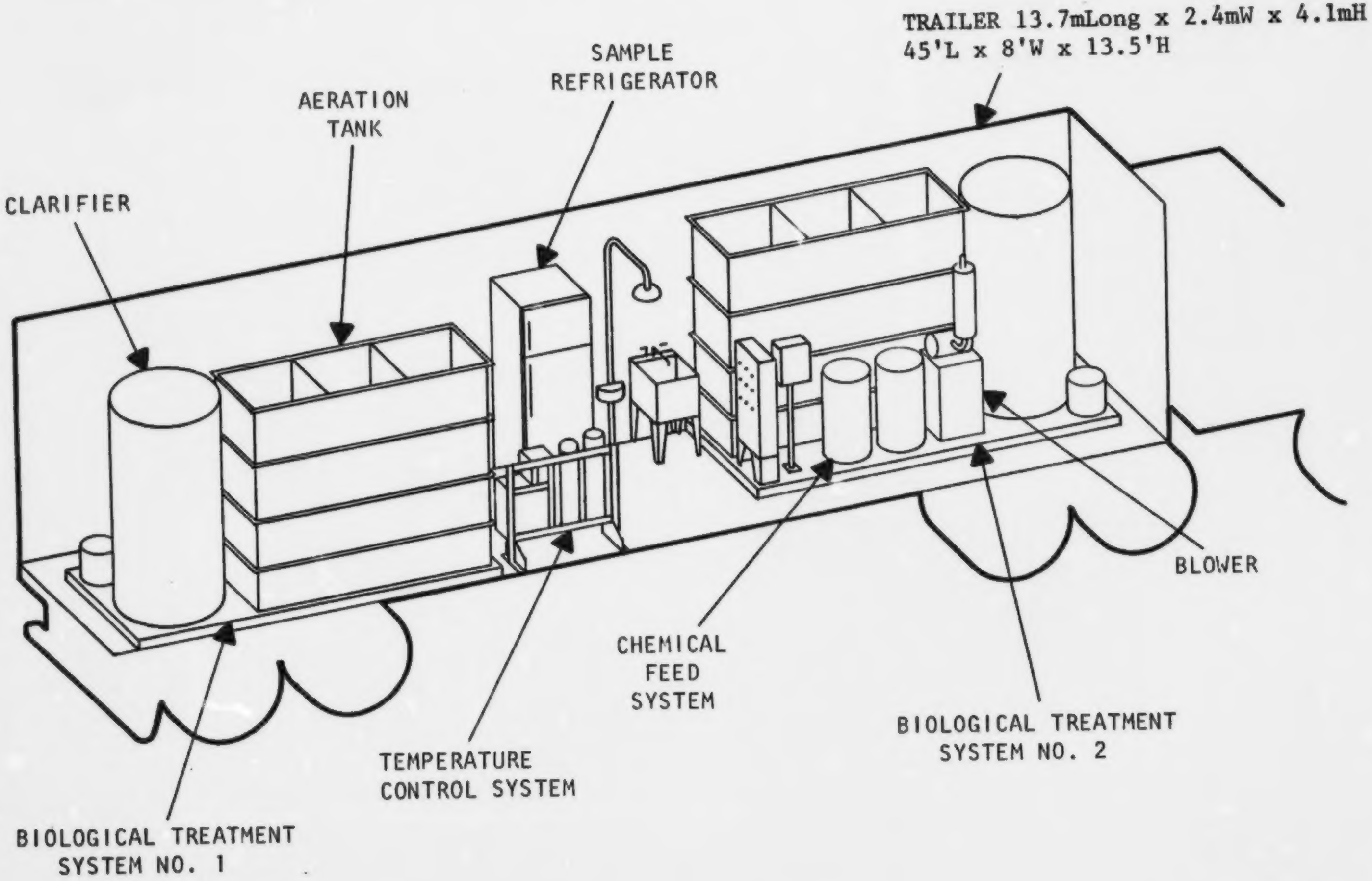

TRAILER 13.7mLong x 2.4mW x 4.1mH
45'L x 8'W x 13.5'H
SAMPLE REFRIGERATOR
AERATION TANK
CLARIFIER
BLOWER
CHEMICAL FEED SYSTEM
BIOLOGICAL TREATMENT SYSTEM NO. 2
TEMPERATURE CONTROL SYSTEM
BIOLOGICAL TREATMENT SYSTEM NO. 1

Figure 3. EPA Mobile Wastewater Treatment System #3 (Biological Trailer).

The smaller EPA biological pilot plant, which was used as the control system, was an activated sludge unit made of acrylic plastic. The aeration tank with a total volume of 180 liters (50 gal) could be partitioned into one to six compartments. For this project, a three cell series arrangement was utilized. The position of the clarifier effluent collector could be varied over a vertical distance of 15.2 cm (6 in.) allowing the clarifier volume to be varied from 22.5 liters (5.9 gal) to 47 liters (12.4 gal). Peristaltic pumps were used to add wastewater to the system and to recirculate settled sludge. The control system was operated at hydraulic and organic loadings similar to the experimental units except that powdered activated carbon was not added to the system. However, caustic soda was added to this unit when necessary, to maintain mixed liquor pH similar to the experimental units. Since this system contained far less volume than those in MWTS #3, heat loss was more significant, especially as the autumn season progressed. In addition, BTS-3 had a different air supply (plant air) which did not add as much heat as the supply for the MWTS #3 (trailer air from blowers). The trailer blowers were throttled to maintain a dissolved oxygen concentration in the aeration tanks of about 2 mg/L. This throttling resulted in a blower air temperature increase to about 66°C (150°F) entering the aeration cells of BTS-1 and BTS-2. This was probably responsible for the temperature differences observed between BTS-1 and BTS-2 as opposed to BTS-3. To correct for temperature differences in BTS-3 thermostatically controlled aquarium heaters were immersed in each of the three mixed liquor (ML) cells. The heaters were set to maintain the control unit aeration basin temperature similar to that measured in the larger pilot units receiving powdered activated carbon.

DESCRIPTION OF THE PHYSICAL-CHEMICAL PILOT PLANTS

The equipment housed in the physical-chemical unit of EPA's MWTS #1 was used to investigate GAC treatment of pharmaceutical plant final effluent. Figure 5 illustrates the pilot plant equipment contained in MWTS #1 including a rapid mix system, flocculator-clarifier, chemical stock tanks, granular activated carbon columns and a multi-media filter. All of these unit processes were utilized during the physical-chemical pilot scale investigation. Presented below is a brief description of the physical-chemical pilot plant equipment. Additional detail can be found in Appendix A.

Description of the Pilot Clarification Equipment

Physical characteristics of the clarifier were:

Overall diameter	1.83 m (6.0 ft)
Net surface area for clarification	2.63 m^2 (28.3 ft^2)
Clarifier volume	2.73 m^3 (96.3 ft^3)
Flocculation volume	0.23 m^3 (8.0 ft^3)
Clarifier detention time	1 hr @ 0.045 m^3/min (12 gpm)
Flocculator "G"s	0-180 m/sec-m (0-180 ft/sec-ft)

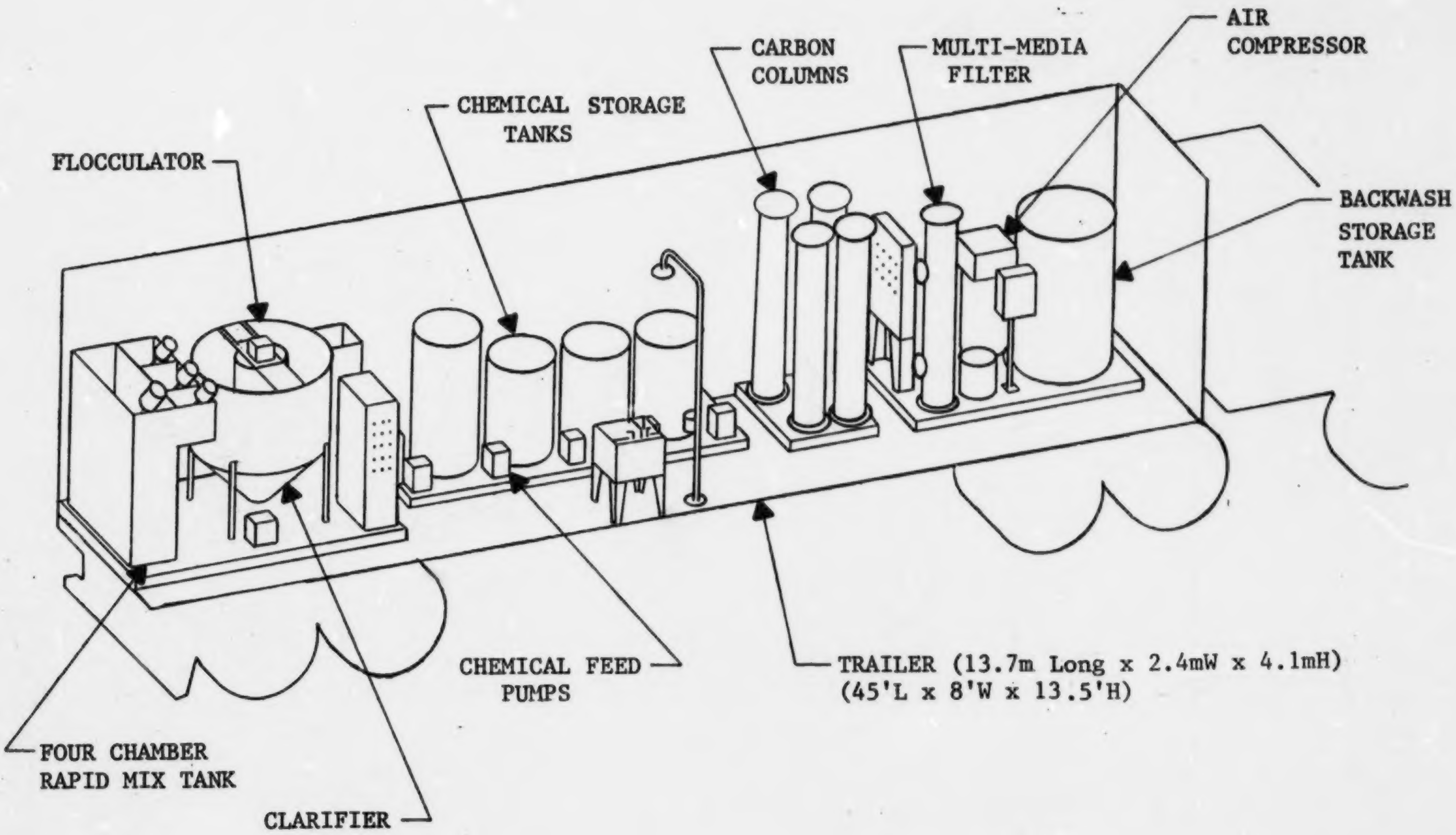

AIR COMPRESSOR
CARBON COLUMNS
MULTI-MEDIA FILTER
CHEMICAL STORAGE TANKS
FLOCCULATOR
BACKWASH STORAGE TANK
CHEMICAL FEED PUMPS
TRAILER (13.7m Long x 2.4mW x 4.1mH)
(45'L x 8'W x 13.5'H)
FOUR CHAMBER RAPID MIX TANK
CLARIFIER

Figure 5. EPA Mobile Wastewater Treatment System #1 (Physical-Chemical Trailer)

Chemicals were pumped into a 379 liter (100 gal) rapid mix tank directly or into the clarifier influent. Alum, caustic soda (used for pH adjustment) and polymer were typically used for chemical addition prior to clarification. The purpose of these chemicals was to act as coagulants to remove suspended solids and to adjust the feed pH.

The flocculation chamber was a cylinder located in the center of the clarifier. Mounted in the center of this chamber was a 30.5 cm (12 in.) diameter turbine flocculator. The blades of the turbine were mounted to produce axial flow. Feed flow was pumped into the draft tube above the turbine. The flocculated wastewater proceeded down the draft tube and into the settling zone. The sludge was removed by a pump activated either manually or by a timer and the clarified effluent was discharged over a weir. Six sampling points were located every 16 cm (6.3 in.) up the side of the clarifier. These taps were used to determine sludge depth.

Description of the Pilot Filtration Equipment

A downflow granular multi-media filter having an effective filtering area of 0.1m^2 (1.0 ft^2) and a pressure rating of 3.5 kg/cm^2 (50 psi) was used in this study. A drawing of the multi-media filter is presented on Figure 6.

As shown on Figure 6, the filter vessel was constructed in two sections. The upper filtration section included flanges at each end for assembly, two 15 cm (6 in.) flanged access ports, and thirteen screened headloss sample taps spaced vertically 10 cm (4 in.) apart. The inside diameter of the upper section was 35 cm (13.6 in.) and the height was 2.1 m (7 ft). The lower section of the filter had a flange at the top for assembly, a drain connection, an effluent connection, backwash connections and a sample tap for filter headloss measurement. A round plate welded to the bottom of the lower section served as a bottom cover and mounting surface for the filter. The top of the upper section was closed by a bolted blind flange having feed inlet and backwash outlet connections.

The upper section of the filter was separated from the lower section by a false bottom, which was bolted between the mating flanges of both sections. The false bottom had three equally spaced threaded holes into which three media strainers were installed. Each strainer had a diameter of 6 cm (2.5 in.) and a number of 0.03 cm (0.01 in.) slots. An air metering tube was bonded to the threaded connection of each strainer and projected below the false bottom from each strainer. Each air metering tube was 15 cm (6 in.) long and 1.3 cm (0.5 in.) in diameter. Four 6 mm (0.25 in.) diameter holes were bored into each air metering tube at equal spaces along the length of each tube.

Flow to the filter was pumped by a 1.5 KW (2 HP), enclosed impeller, centrifugal pump. Backwash water (filtered effluent) was pumped from a 1,900 liter (500 gal) tank by a 0.6 KW (3/4 HP), enclosed impeller, centrifugal pump and an air compressor was provided for backwash air scour.

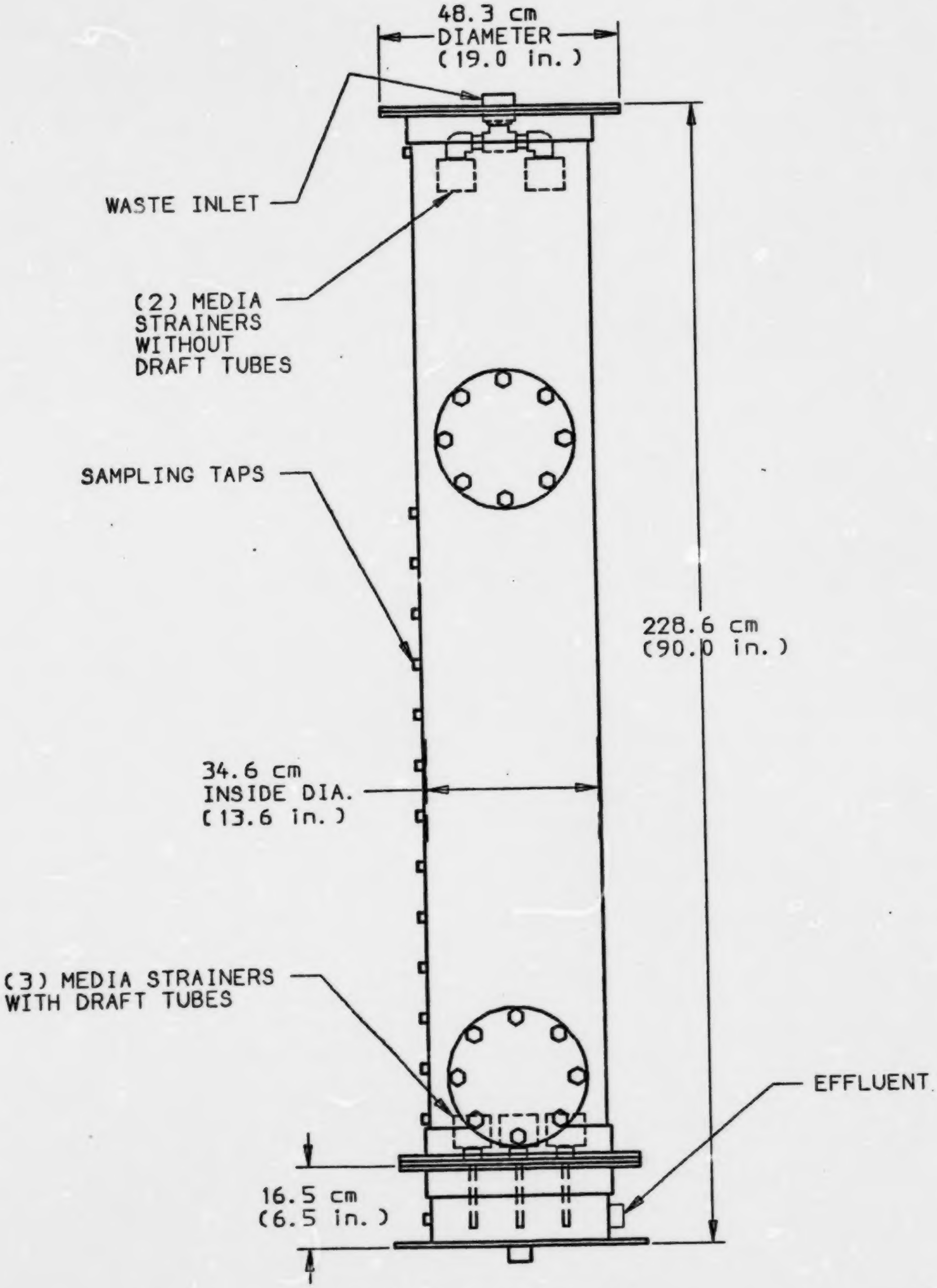

48.3 cm
DIAMETER
(19.0 in.)
WASTE INLET
(2) MEDIA STRAINERS WITHOUT DRAFT TUBES
SAMPLING TAPS
228.6 cm
(90.0 in.)
34.6 cm
INSIDE DIA.
(13.6 in.)
(3) MEDIA STRAINERS WITH DRAFT TUBES
EFFLUENT
16.5 cm
(6.5 in.)

Figure 6. Pilot System Multi-media Filter.

The purpose of the pilot filter was to provide additional pretreatment for the removal of TSS. In addition, there was interest in collecting information on filter efficiency for removal of selected parameters.

The following field testing conditions were selected.

1. Filtration Rate: The filtration rate was held constant at 120 L/min-m^2 (3 gpm/ft^2) from 9/8 to 10/25 and at 100 L/min-m^2 (2.5 gpm/ft^2) from 10/25 to the end of the testing period (12/4).

2. Feed Characteristics: This variable was determined by the process preceding the filter. During the study, the multi-media filter processed chemically treated clarifier effluent.

3. Filter Media: Filter media consisted of two grades of garnet sand covered by silica sand and a top layer of anthracite coal. A description of these is presented below.

Media Type	Depth	Effective Size, mm	Uniformity Coefficient
Anthracite	51 cm (20 in.)	0.94	1.60
Silica sand	38 cm (15 in.)	0.47	1.34
Fine garnet sand	15 cm (6 in.)	0.113	1.42
Coarse garnet sand	15 cm (6 in.)	0.37	1.29

4. Backwash: Backwashing was initiated both manually and automatically during the study. The procedure was to first draw the water level down 31 cm (12 in.) from the overflow. Next, backwashing was initiated at 200 L/min-m^2 (5 gpm/ft^2) while simultaneously agitating with air at 1.5 standard m^3/min-m^2 (5 scfm/ft^2) for two minutes. After turning off the air, service water was used to backwash the filter at 610 L/min-m^2 (15 gpm/ft^2) for ten minutes.

5. Mode of Filter Operation: All tests were run under pressure with constant hydraulic flow.

6. Terminal Headloss: The pilot filter was operated at a pressure of about 2 kg/cm^2 (25 psig). Terminal headloss was assumed to occur at a differential pressure of about 1 kg/cm^2 (15 psig) (4).

The filter was operated continuously throughout the study. Each interval between backwashings was called a run and assigned a number. Run lengths were generally determined by the headloss buildup and were quite variable, ranging from 3 to 100 hours long. At the beginning of each run the flow controller was set to the desired rate and initial headloss readings were taken. Periodically during the run, overall headloss was recorded and turbidity of the feed and filtrate was measured. Headloss profiles through the media were recorded at intervals during the run and at termination. Following termination of a run, the filter was backwashed and prepared for the next run. Samples of feed and filtrate were typically composited over 24 hour periods. However, no sampling was performed during periods of backwash. The daily samples were submitted for laboratory analysis.

Multi-media Filter Potential Design Problems--

During the backwash cycle, the filter was allowed to drain down to the backwash collection outlet. Air was then introduced under pressure into the filter at the backwash connection below the false bottom. The air pressure forced the filtrate remaining in the lower section of the filter up the air metering tubes. When the air had displaced sufficient filtrate, the orifices in the air metering tubes were uncovered, thereby permitting air bubbles to enter the upper section of the filter. The headloss of the air passing through the air metering tube orifices continued to drive filtrate residual and air bubbles upward until the static pressure in the filter was equal to the headloss across all uncovered orifices. If the orifices were at equal elevations, an equal amount of air would be metered into each media strainer. The air metering tubes thus served to automatically distribute the air for effective air scouring of the media.

However, it is possible for the air metering tube orifices to become clogged. Also, the filter must be properly leveled. In either case, an unequal distribution of air scour could upset the media sufficiently to preclude the layered settling of the media following backwashing. Further, it is also possible for one or more of the media to become clogged or "mudballed". This condition would also cause unequal flow distribution of backwash air and water. Although not utilized in this project, future studies might consider the use of pea gravel to be placed over the media strainers to a depth of 15 cm (6 in.). This action will assist flow distribution while trapping the filter media, which could clog the media strainer slots.

Description of the Pilot Activated Carbon Equipment

The MWTS #1 was equipped with a granular activated carbon adsorption system which consisted of four pressure vessels, each having an effective area of 0.1 m^2 (1.0 ft^2) and a pressure rating of 3.5 kg/cm^2 (50 psi). A drawing of a typical activated carbon vessel is presented on Figure 7. For this study, the four adsorbers were connected in series.

Each pressure vessel was constructed in two sections, as shown on Figure 7. The upper section included flanges at both ends for assembly, two 15 cm (6 in.) flanged access ports and 7 screened sample taps spaced vertically 30 cm (12 in.) apart. The diameter of the upper section was 34.6 cm (13.6 in.) and the height was 2.1 m (7 ft). The lower section of each vessel included a flange for assembly, a sample tap, a drain connection, an effluent outlet and backwash inlet connections. A round plate welded to the bottom of the lower section served as the bottom cover and as a mounting surface for each vessel. A round plate bolted to the top of the upper section of each column served as the top cover and contained connections for inlet and outlet, and a safety relief valve.

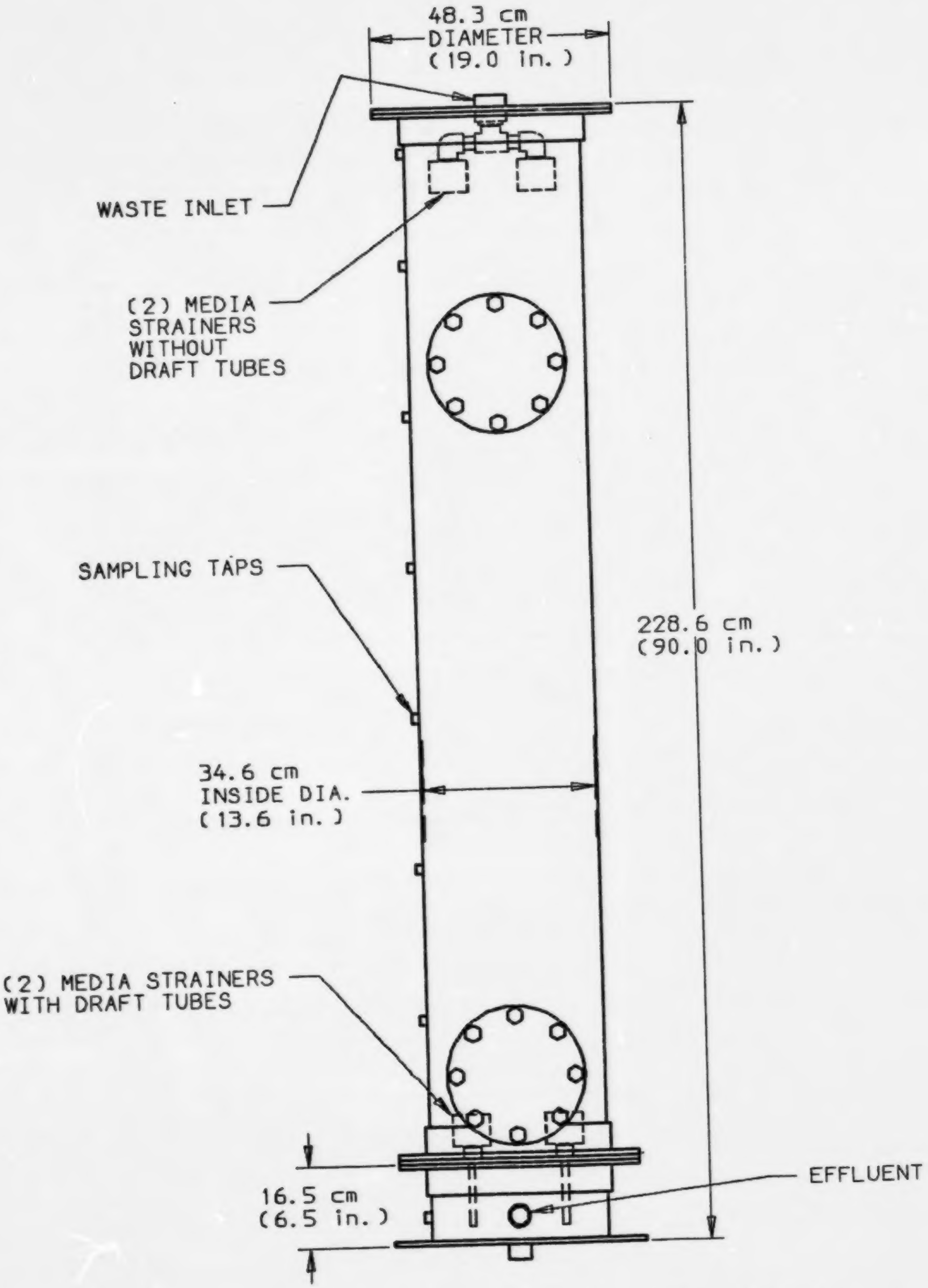

48.3 cm
DIAMETER
(19.0 in.)
WASTE INLET
(2) MEDIA STRAINERS WITHOUT DRAFT TUBES
SAMPLING TAPS
228.6 cm
(90.0 in.)
34.6 cm
INSIDE DIA.
(13.6 in.)
(2) MEDIA STRAINERS WITH DRAFT TUBES
EFFLUENT
16.5 cm
(6.5 in.)

Figure 7. Pilot System Activated Carbon Column (One of Four).

The upper section of each activated carbon vessel was separated by a false bottom which was bolted between the mating flanges of both sections. The false bottom had two threaded holes into which were installed two media strainers without air metering tubes. The strainers had a diameter of 6 cm (2.5 in.) and a number of 0.03 cm (0.01 in.) slots. The feed inlet at the top of each vessel was equipped with two media strainers without air metering tubes, mounted on a pipe manifold. Pressure gauges were mounted at the top and bottom of each vessel to monitor headloss across the carbon bed.

Virgin carbon was used in each of the four columns. Insufficient time was available to optimize the selection of carbon. Calgon's Filtrasorb 300 was chosen due to its successful application to similar wastestreams. Specifications pertinent to the activated carbon used in the pilot study are presented in Table 1.

The wastewater pumped to the activated carbon vessels was clarified and filtered pharmaceutical plant final effluent. A self-priming pump was used to pump influent wastewater into the activated carbon vessels in either the downflow (Run #1) or upflow (Run #2) modes. For this study, both modes were evaluated under the conditions listed in Table 2.

Potential design problems existed with the activated carbon column backwashing system. While initially backwashing the carbon, the inlet strainers may have clogged with the fine carbon particles. Headloss may have built up until backwashing was no longer possible. Further, if all fines were not removed during the initial backwash, the potential existed on

TABLE 1. ACTIVATED CARBON DESCRIPTION AND SPECIFICATIONS

Parameter		Description/Specifications
Wastewater Source	-	Chemically treated, clarified and filtered pharmaceutical plant effluent
Carbon Type	-	Filtrasorb 300
Carbon Manufacturer	-	Calgon
System Configuration	-	Fixed Bed
Number of Absorbers	-	4
Adsorber Diameter	-	36 cm (14 in.)
Carbon Density, Dry, kg/m^3 (lb/ft^3)	-	500 (31)
Carbon Density, Backwashed and drained, kg/m^3 (lb/ft^3)	-	430 (27)

subsequent backwashes for a reclassification of the carbon bed. This may have led to erroneous analytical results from samples collected immediately after backwash. Adequate backwash flow distribution may also have been difficult without an aggregate media support. This potential problem was recognized and corrected for in GAC Run #2 as indicated in Table 2.

TABLE 2. ACTIVATED CARBON OPERATING CONDITIONS

	Run # 1	Run #2*
Study Period	9/11 - 10/12	10/24 - 12/4
System Operation	Downflow, Series	Upflow, Series
Initial Carbon Depth, m (in.)		
Column No. 1	1.68 (66.3)	1.29 (50.8)
2	1.66 (65.3)	1.28 (50.5)
3	1.70 (67.0)	1.29 (50.8)
4	1.67 (65.8)	1.30 (51.0)
Total	6.71 (264.4)	5.16 (203.1)
Final Carbon Depth, m (in.)		
Column No. 1	1.72 (67.8)	1.27 (50.0)
2	1.72 (67.8)	1.22 (48.0)
3	1.66 (65.3)	1.30 (51.0)
4	1.65 (65.0)	1.27 (50.0)
Total	6.75 (265.9)	5.06 (199.0)
Average Linear Flow Rate L/min-m^2 (gpm/ft^2)	65 (1.6)	36.7 (0.9)
Initial Weight of Carbon in System, kg (lbs)	271 (596)	206 (452)
Contact Time, min		
Empty bed contact time per column	26 for 1.7m (5.5 ft) carbon bed depth	35 for 1.3m (4.2 ft) carbon bed depth
Total empty bed contact time	104	140

*Each of the four carbon columns was loaded with 15 cm (6 in.) of washed #7 pea gravel having an effective size of 1.3 cm (0.5 in.) and a uniformity coefficient of 1.0 and 15 cm (6 in.) of washed concrete sand having an effective size of approximately 0.5 mm and a uniformity coefficient of 1.6.

SECTION 6

PILOT PROJECT TEST PLAN

INTRODUCTION

This section discusses test plans that were developed for both the biological and the physical-chemical pilot plant studies. The original test plans for this project were prepared in August, 1984; however, after start-up in September, 1984, some modifications to the original plans were necessary. These are discussed in detail later in this section.

The pilot equipment was typically operated 24 hours per day, 7 days per week during the study. Two operators were on-site 10-12 hours each day to take readings, record pertinent data and make operational checks on the system. Composite sampling was performed using automatic samplers set to draw one constant volume sample each 30 minutes over a 24 hour period. Grab samples on the granular activated carbon system were collected each day. All chemical feed rates, waste flows, sludge wastage, column pressures, temperatures, etc. were recorded on field data sheets in duplicate. Settling tests and sludge thickening tests were routinely performed in the field. All information was entered in ink in a permanently bound field notebook.

Throughout the report, reference is made to various days (or sample collection periods) of the study (ex. Day N). Day 1 of the study began on September 7. Day N is the 24 hour sample that was started on Day N and taken off on Day N+1.

BIOLOGICAL TEST PLAN

The objective of the biological treatment study was to evaluate the effectiveness of powdered activated carbon addition to the aeration basin to further reduce effluent concentrations of TCOD. Three activated sludge units were operated in parallel. Two of the systems were fed different concentrations of powdered activated carbon. The third unit was used as a control. The following pages discuss the equipment operation, operating parameters, test schedule, field monitoring activity and sampling and analytical activity concerned with the biological systems.

Equipment Operation

Raw pharmaceutical wastewater collected just before entering the full-scale aeration basins was used as feed to the biological systems. This flow consisted of neutralized/equalized pharmaceutical manufacturing wastewater and macerated and chlorinated sanitary wastewater (< 6% of flow).

A schematic diagram of the biological treatment units is shown on Figure 8. The raw wastewater was pumped to a 114 L (30 gal) mixing tank in the treatment trailer. Feed was pumped from this tank directly to BTS-1 and BTS-2. Flow rate to these two units was controlled by a throttling valve. Feed to BTS-3, located in the adjacent support trailer, was pumped to a 76 L (20 gal) mixing tank located along BTS-3. A small positive displacement pump was used to transfer the wastewater from this tank to BTS-3. Flow rates to all units were measured by the volume/stopwatch method.

PAC was added as a slurry to cell 1 of BTS-1 and BTS-2. Each unit (BTS-1 and BTS-2) was supplied from its own slurry tank. PAC slurry was metered to each unit by means of a positive displacement pump and the addition rate was measured by the volume/stopwatch method. No PAC was added to BTS-3.

Air flow to each aeration tank cell of each aeration basin was adjusted to maintain the minimum targeted dissolved oxygen content of 2 mg/L. Dissolved oxygen measurements were made in each cell at least once per day to aid in making necessary air flow adjustments. At times, the 2 mg/L oxygen concentration could not be maintained using the maximum air available.

The mixed liquor flowed by gravity from the aeration tanks to circular center feed clarifiers (BTS-1 and BTS-2). A pipe flushing mechanism was installed to periodically clear the transfer pipe of settled solids and prevent the build up of headloss. Once every eight to ten minutes, a motorized valve at the aeration tank end of the transfer pipe closed and a pump was used to pump clarifier effluent through the transfer line to the clarifier for about 10 seconds. The pump turned off and the motorized valve reopened to allow mixed liquor to flow again to the clarifier. This flushing sequence had no visual effect on the clarifier effluent quality. At times, in spite of the pipe flushing mechanism, the mixed liquor transfer pipes became partially blocked causing the aeration tank to overflow. Mixed liquor flow from the BTS-3 aeration tank to the clarifier also flowed by gravity. No transfer pipe flushing was needed for this unit.

Round center feed clarifiers were used to clarify the mixed liquor for BTS-1 and BTS-2. Clarifier effluent flowed by gravity to a sampling container and then to a drain. Each clarifier was equipped with a scraper chain to agitate the settled sludge in the conical clarifier bottom. This mechanism was rotated by hand several times each day. Settled sludge was pumped from the clarifier to cell 1 of each unit (BTS-1 and BTS-2) using a positive displacement pump operated intermittently by a timer. The pump flow rate was measured by the volume/stopwatch method. This flow rate plus the on/off pump cycle time was used to calculate the return sludge flows. The average return sludge flow was adjusted by changing the pump cycle time.

A plastic clarifier in the shape of an inverted four sided pyramid was used to clarify the mixed liquor from BTS-3. Because of poor settling of

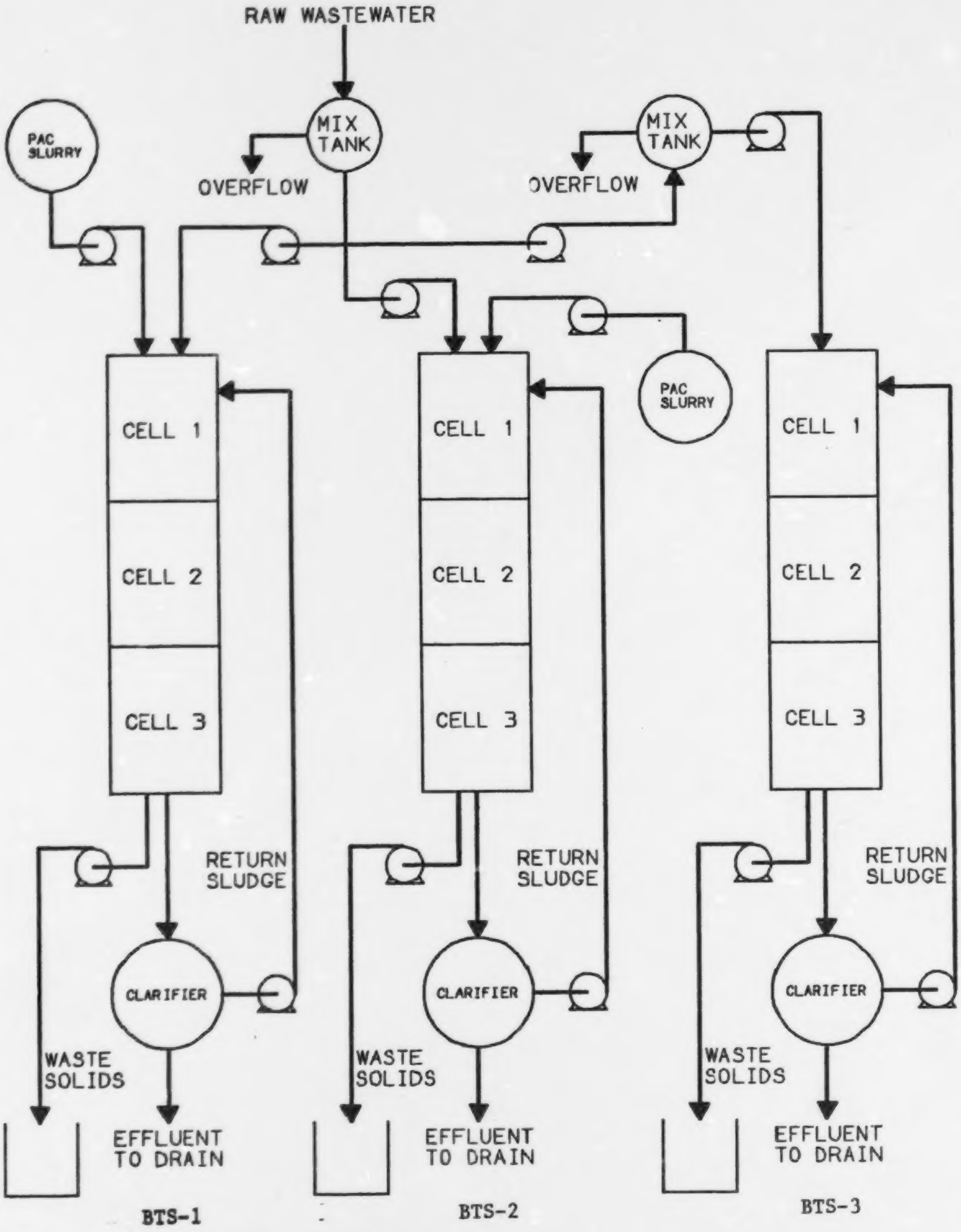

RAW WASTEWATER
MIX TANK
OVERFLOW
PAC SLURRY
MIX TANK
OVERFLOW
CELL 1
CELL 2
CELL 3
RETURN SLUDGE
CLARIFIER
WASTE SOLIDS
EFFLUENT TO DRAIN
BTS-1
CELL 1
CELL 2
CELL 3
PAC SLURRY
RETURN SLUDGE
CLARIFIER
WASTE SOLIDS
EFFLUENT TO DRAIN
BTS-2
CELL 1
CELL 2
CELL 3
RETURN SLUDGE
CLARIFIER
WASTE SOLIDS
EFFLUENT TO DRAIN
BTS-3

Figure 8. Schematic Flow Diagram of the Biological Treatment Systems.

the BTS-3 mixed liquor, a second clarifier was installed in parallel shortly after start-up. The second clarifier was removed from the system on October 13 (Day 36) after a schedule of frequent (three times per day) scraping of clarifier walls was started and the performance of the clarifier improved. Sludge was returned to cell 1 of BTS-3 by continuous operation of a positive displacement peristaltic pump. Flow rate was measured by the volume/stopwatch method and controlled by changing the pump speed.

Solids were wasted from units BTS-1 and BTS-2 by continuously pumping mixed liquor from cell 3 of each unit to a waste sludge holding tank (one for each unit) using positive displacement peristaltic pumps. Flow rates were measured by the volume/stopwatch method and controlled by changing pump speed. The volume of waste mixed liquor was measured in each holding tank once a day to determine the average daily wasting rate. After measuring and sampling, each holding tank was emptied for the next day. A peristaltic pump was operated intermittently using a timer to waste mixed liquor from cell 3 of BTS-3. Flow measurement, control and emptying of the waste solids holding tank were similar to operations for BTS-1 and BTS-2.

As discussed previously in Section 5, BTS-3 used a lower temperature air source (plant air) than that of BTS-1 and BTS-2 (trailer air). In order to keep the temperatures in all test units at a comparable level, aquarium heaters and heating tapes were installed on October 2 in each aeration cell of BTS-3. Temperatures were monitored daily and controlled in BTS-3 so as to be similar to the temperatures in BTS-1 and BTS-2.

It was necessary during the test period to occasionally add caustic soda to the mixed liquor to maintain minimum pH levels during periods of nitrification. Sodium hydroxide solution was also added manually to each cell to counteract sudden increases in feed acidity due to acid spills in the processing plant. Gradual changes in mixed liquor pH were controlled by the continuous addition of dilute solutions of sodium hydroxide to cell 3 of each aeration tank. A positive displacement chemical feed pump was used for BTS-1 and BTS-2 and a gravity feed drip system was used for BTS-3. Caustic soda addition was started when the mixed liquor pH dropped below 7 and was discontinued when the pH returned to 7.

Operating Parameters

The key operational parameters selected for the pilot plants were similar to those being used on the full-scale plant just prior to the study. Aeration tank hydraulic retention time (HRT) and solids retention time (SRT) were to be maintained at 3 days and 10 days, respectively, for all units. Two test periods were planned, with 200 and 800 mg PAC per liter of feed added to BTS-1 and BTS-2, respectively, in the first period and 400 and 1200 mg PAC per liter of feed added to BTS-1 and BTS-2, respectively, in the second period. After evaluation of the results from the first test period, the target PAC dosages for the second period were changed to 500 mg/L and 1500 mg/L, respectively. The planned operating parameters are listed in Table 3.

Each test period was preceded by a ten day period when the PAC concentration of the mixed liquor was brought up to the expected equilibrium level followed by a period of acclimation. PAC was fed continuously plus it was added daily in slurry form (ten percent solids) to each aeration tank cell of units BTS-1 and BTS-2 for ten days. The amounts added each day are listed in Table 4.

Test Schedule

The operation of the pilot plants was planned to be performed in the following phases:

Phase	Maximum Interval	Cumulative Time
1. Start-up	10 days	5 to 10 days
2. Acclimation	30 days	35 to 40 days
3. Intensive testing	14 days	49 to 54 days
4. Transition and acclimation	30 days	79 to 84 days
5. Intensive testing	14 days	93 to 98 days

TABLE 3. PLANNED OPERATING PARAMETERS FOR BIOLOGICAL PILOT PLANTS

	Pilot Plant		
	BTS-1	BTS-2	BTS-3
Aeration Volume, liters	5940	5560	189
Raw Feed Flow, L/min	1.38	1.29	0.044
Aeration Detention Time, days	3	3	3
Sludge Retention Time, days	10	10	10
Waste Mixed Liquor Flow,* L/min	0.41	0.39	0.013
First Test Period:			
PAC Addition, mg/L of feed	200	800	0
PAC Slurry Flow, ml/min	18.4	18.4	0
PAC Slurry Concentration, %	1.5	5.6	0
Second Test Period:			
PAC Addition, mg/L of feed	500	1500	0
PAC Slurry Flow, ml/min	31.6	31.6	0
PAC Slurry Concentration, %	2.18	6.12	0

*Assuming effluent suspended solids are negligible.

In addition, three to five days were allowed for equipment siting and hook-up at the start of testing and 3 days were allowed for disassembly at the end of testing.

Phase 1. Start-up--

All aeration tank cells and clarifiers were filled with mixed liquor from the full scale treatment plant. Aeration was started immediately. The appropriate wastewater feed flow rates were then started. Sludge recycle pumps were started and mixed liquor wastage rates were set for the targeted 10 day SRT. The units were operated until apparent steady state (as measured by daily MLSS and effluent SCOD concentration) conditions were reached so that the three units could be compared before the start of PAC addition.

TABLE 4. DAILY AMOUNTS OF CARBON ADDED TO BTS-1 AND BTS-2

	Aeration Cell	Cell Volume, L	PAC Added per Day, g	
			Days 1-9	Day 10
Preceding First Test Period	BTS-1 Cell 1	1981	75	77
	BTS-1 Cell 2	1981	75	75
	BTS-1 Cell 3	1981	75	81
	BTS-2 Cell 1	1981	320	191
	BTS-2 Cell 2	1981	320	213
	BTS-2 Cell 3	1594	256	205
Preceding Second Test Period	BTS-1 Cell 1	1981	120	87
	BTS-1 Cell 2	1981	120	79
	BTS-1 Cell 3	1981	120	83
	BTS-2 Cell 1	1981	278	209
	BTS-2 Cell 2	1981	278	196
	BTS-2 Cell 3	1594	222	178

Phase 2. Acclimation--

Continuous addition of PAC was started to BTS-1 and BTS-2 at concentrations of 200 mg/L and 800 mg/L, respectively. Single doses of PAC (as a ten percent slurry) were also added to each aeration cell of BTS-1 and BTS-2 each day for the first ten days to reach the calculated equilibrium PAC concentration. Operation continued until apparent steady state conditions were reached in the experimental units based on daily MLSS and effluent SCOD concentrations.

Phase 3. Intensive Testing--

Operation continued under the same operating conditions. Frequency of operational measurements was increased. Mixed liquor settling tests and oxygen uptake rate tests were performed. An intensive analytical schedule was performed for two weeks.

Phase 4. Transition and Acclimation--

Continuous addition of PAC to units BTS-1 and BTS-2 was increased to 500 mg/L and 1500 mg/L, respectively. Doses of slurried PAC were added to each aeration cell each day for ten days to reach the calculated equilibrium PAC concentration. Operation continued until apparent steady state conditions were reached based on daily MLSS and effluent SCOD concentrations.

Phase 5. Intensive Testing--

The two week intensive testing performed during Phase 3 was to be repeated.

Field Monitoring Activity

The following activities were performed:

1. Measure and record flows and chemical dosages daily. Adjust as necessary

2. Measure and record dissolved oxygen in each aeration cell once daily. Adjust air flow rate, if necessary.

3. Measure and record temperature and pH of feed, mixed liquor (each aeration cell) and clarifier effluent (each unit) daily. Adjust heaters in BTS-3 as necessary.

4. Check chemical solutions and prepare new solutions as needed.

5. Obtain sample of mixed liquor from the last cell of each unit and perform settling test.

6. Determine amount of solids wasted by analyzing TSS of a sample of each batch of waste mixed liquor discharged from the waste solids holding tanks and measuring the volume discharged.

7. Coordinate the acquisition of pilot plant grab and composite samples. Maintain samplers and prepare samplers for next sampling event.

8. Perform standard bench scale tests as an aid in monitoring and controlling each system. Bench scale polymer dosage tests were performed to evaluate the effect of polymer treatment on settling characteristics. The following tests were performed during each intensive test period to aid in the design of full-scale equipment: mixed liquor oxygen uptake rate, solids settling rate, and sludge volume.

9. Perform necessary maintenance and repair of treatment equipment.

Flow, pH, temperature and dissolved oxygen measurements were performed at least twice each day during the intensive test periods.

Sampling and Analytical Activity

Sampling and analytical procedures that were best done during or immediately after sampling were performed in-situ. The remaining analytical work was submitted to the field laboratory located adjacent to the pilot plant equipment. Analyses were either performed in the field lab or samples were packaged and shipped to the remote laboratory.

The sampling locations are shown on Figure 9. Composite samples were taken of the raw feed wastewater (B) and of the clarifier effluents (F1, F2 and F3) using automatic sampling equipment. The samplers sampled once every half hour. Sample containers were iced during sample collection. Composite samples of wasted mixed liquor (G1, G2 and G3) were obtained from the waste solids holding tanks immediately before the daily accumulation of solids was measured and discarded. The contents of each tank were vigorously stirred while taking the sample. Samples of PAC slurry (H1 and H2) were initially taken directly from the slurry stock tanks for suspended solids analysis. The PAC slurry analytical results varied widely. After October 23 (Day 46), a sample of the entire flow of PAC slurry entering cell 1 of each unit for a 30 second period was placed directly into an analytical dish, dried and weighed for PAC.

Temperature and dissolved oxygen measurements were performed in-situ. Temperature measurements were taken of the mixed liquor in each aeration tank cell and of the clarifier effluent. Dissolved oxygen measurements were taken of the mixed liquor in each aeration tank cell using a Weston and Stack dissolved oxygen meter. Measurements of pH were performed on grab samples of mixed liquor and clarifier effluent immediately after sampling. Composite samples of feed wastewater (B), waste mixed liquor (G1, G2 and G3) and clarifier effluents (F1, F2 and F3) were also analyzed for pH.

TCOD, SCOD, total biochemical oxygen demand, (TBOD), soluble biochemical oxygen demand (SBOD), nitrogen inhibited BOD, (NIBOD), soluble NIBOD (NISBOD), TSS and volatile suspended solids (VSS) analyses were

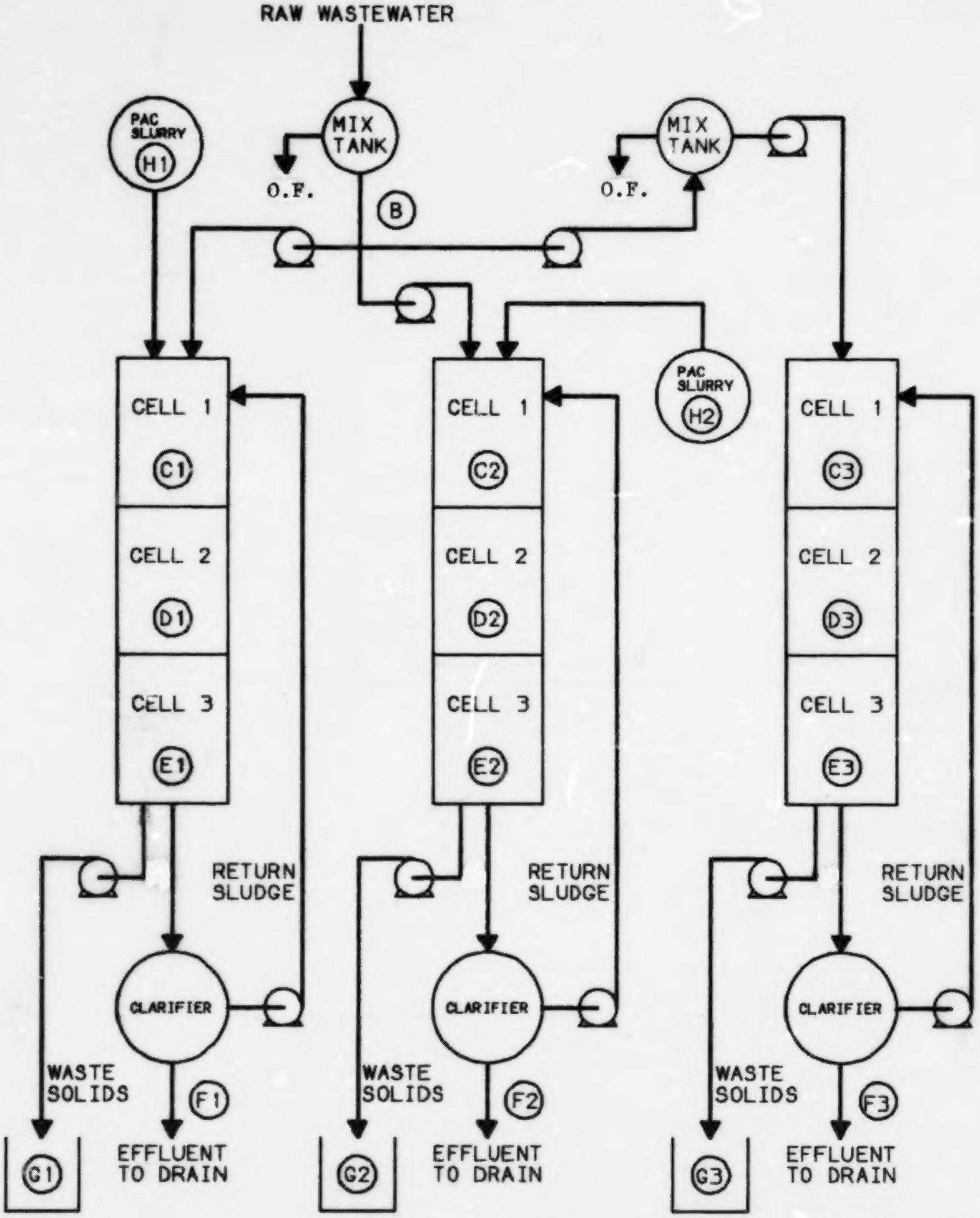

RAW WASTEWATER
PAC SLURRY
H1
MIX TANK
O.F.
B
MIX TANK
O.F.
PAC SLURRY
H2
CELL 1
C1
CELL 2
D1
CELL 3
E1
CELL 1
C2
CELL 2
D2
CELL 3
E2
CELL 1
C3
CELL 2
D3
CELL 3
E3
RETURN SLUDGE
RETURN SLUDGE
RETURN SLUDGE
CLARIFIER
CLARIFIER
CLARIFIER
WASTE SOLIDS
F1
WASTE SOLIDS
F2
WASTE SOLIDS
F3
G1
EFFLUENT TO DRAIN
G2
EFFLUENT TO DRAIN
G3
EFFLUENT TO DRAIN

Figure 9. Schematic of Biological Pilot Plant Sampling Locations.

performed at the study site. Additional analyses for total organic carbon (TOC), soluble TOC (STOC), chloride (Cl), nutrients (nitrogen series and phosphorus) and special organic analyses were performed at a remote laboratory.

The sampling and analysis schedule for the start-up and acclimation phases (Phases 1, 2 and 4) is shown in Table 5. The schedule for the intensive testing periods (Phases 3 and 5) is shown in Table 6.

TABLE 5. PLANNED SAMPLING AND ANALYSIS SCHEDULE FOR START-UP AND ACCLIMATION PERIODS (PHASES 1, 2 & 4)

Parameter	Minimum Frequency	Sample Type	Sample Point
TSS	Daily	Grab	H1, H2
TSS	Daily	Comp	B,F1,F2,F3,G1, G2,G3
VSS	3/Week	Comp	B,F1,F2,F3,G3
TBOD	3/Week, 1st wk 1 Week, afterward	Comp	B B
NISBOD*	3/Week, 1st wk 1/Week, afterward	Comp	F1,F2,F3 F1,F2,F3
NIBOD	3/Week, 1st wk 1/Week, afterward	Comp	F1,F2,F3 F1,F2,F3
TCOD	Daily	Comp	B,F1,F2,F3
SCOD*	Daily	Comp	F1,F2,F3
TOC**	3/Week	Comp	B,F1,F2,F3
STOC**	3/Week	Comp	F1,F2,F3
Chloride	Daily - 1st wk 2/Week, thereafter	Comp	B B

*Soluble BOD, COD and TOC measured on filtrate from filtration through 0.45 micron membrane filters.

**During Phase 4, the nitrogen series was substituted for TOC and STOC.

PHYSICAL-CHEMICAL TEST PLAN

The objective of the physical-chemical pilot study was to evaluate the performance of granular activated carbon for the removal of SCOD from a biologically treated pharmaceutical plant effluent. Solids removal technologies (clarification and filtration) were utilized for pretreatment of the wastewater prior to carbon adsorption. Data were generated on removal efficiencies for selected parameters from the pretreatment technologies, although no attempt was made to develop detailed scale-up information. A schematic of the physical-chemical pilot plants is shown on Figures 10 and 11. All grab and composite sampling points are illustrated on the figures. Figure 10 represents the treatment train evaluated from 9/11 to 10/12. During this phase of testing, the first run on the granular

TABLE 6. PLANNED SAMPLING AND ANALYSIS SCHEDULE FOR INTENSIVE TESTING PERIODS (PHASES 3 and 5)

Parameter	Minimum Frequency	Sample Type	Sample Points
TSS	Daily	Grab	H1,H2
TSS	Daily	Comp	B,F1,F2,F3,G1,G2,G3
VSS	Daily	Comp	B,G3,G1,F2,F3
TBOD	3/Week	Comp	B
NIBOD	3/Week	Comp	F1,F2,F3
NISBOD*	3/Week	Comp	F1,F2,F3
TCOD	Daily	Comp	B,F1,F2,F3
SCOD*	Daily	Comp	F1,F2,F3
TOC	Daily	Comp	B,F1,F2,F3
STOC*	Daily	Comp	F1,F2,F3
Chloride	2/Week	Comp	B
Specific Organic Compounds	5/Period	Comp	B,F1,F2,F3

* Soluble parameters measured on filtrate from filtration through 0.45 micron membrane filters.

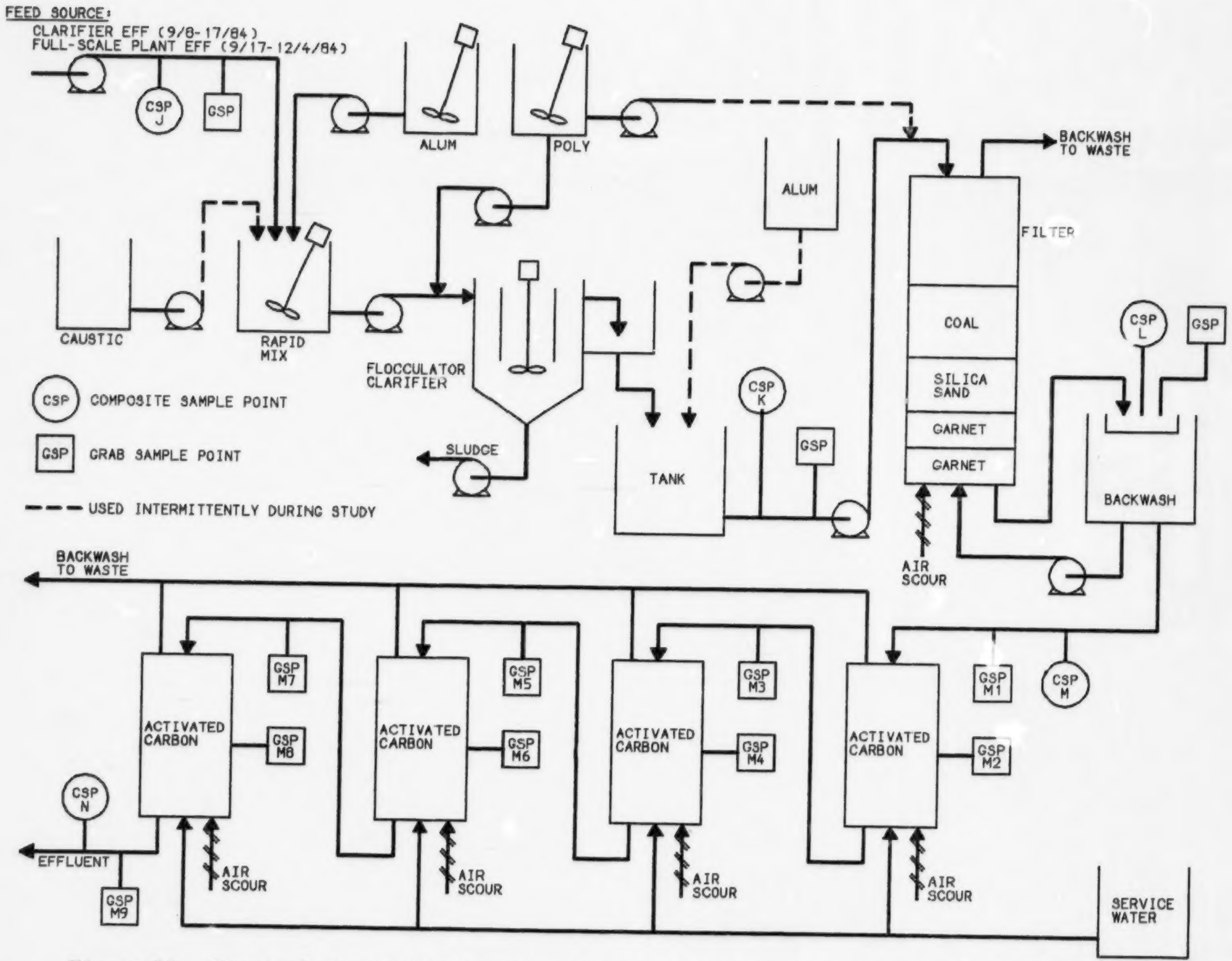

FEED SOURCE:
CLARIFIER EFF (9/8-17/84)
FULL-SCALE PLANT EFF (9/17-12/4/84)
CSP J
GSP
ALUM
POLY
CAUSTIC
RAPID MIX
FLOCCULATOR CLARIFIER
SLUDGE
ALUM
TANK
CSP K
GSP
BACKWASH TO WASTE
FILTER
COAL
SILICA SAND
GARNET
GARNET
AIR SCOUR
CSP L
GSP
BACKWASH
CSP COMPOSITE SAMPLE POINT
GSP GRAB SAMPLE POINT
USED INTERMITTENTLY DURING STUDY
BACKWASH TO WASTE
GSP M1
CSP M
ACTIVATED CARBON
GSP M2
GSP M3
ACTIVATED CARBON
GSP M4
GSP M5
ACTIVATED CARBON
GSP M6
GSP M7
ACTIVATED CARBON
GSP M8
AIR SCOUR
AIR SCOUR
AIR SCOUR
AIR SCOUR
CSP N
EFFLUENT
GSP M9
SERVICE WATER

Figure 10. Physical-Chemical Pilot Plant Schematic Used During GAC Run No. 1 (9/11 to 10/12/84).

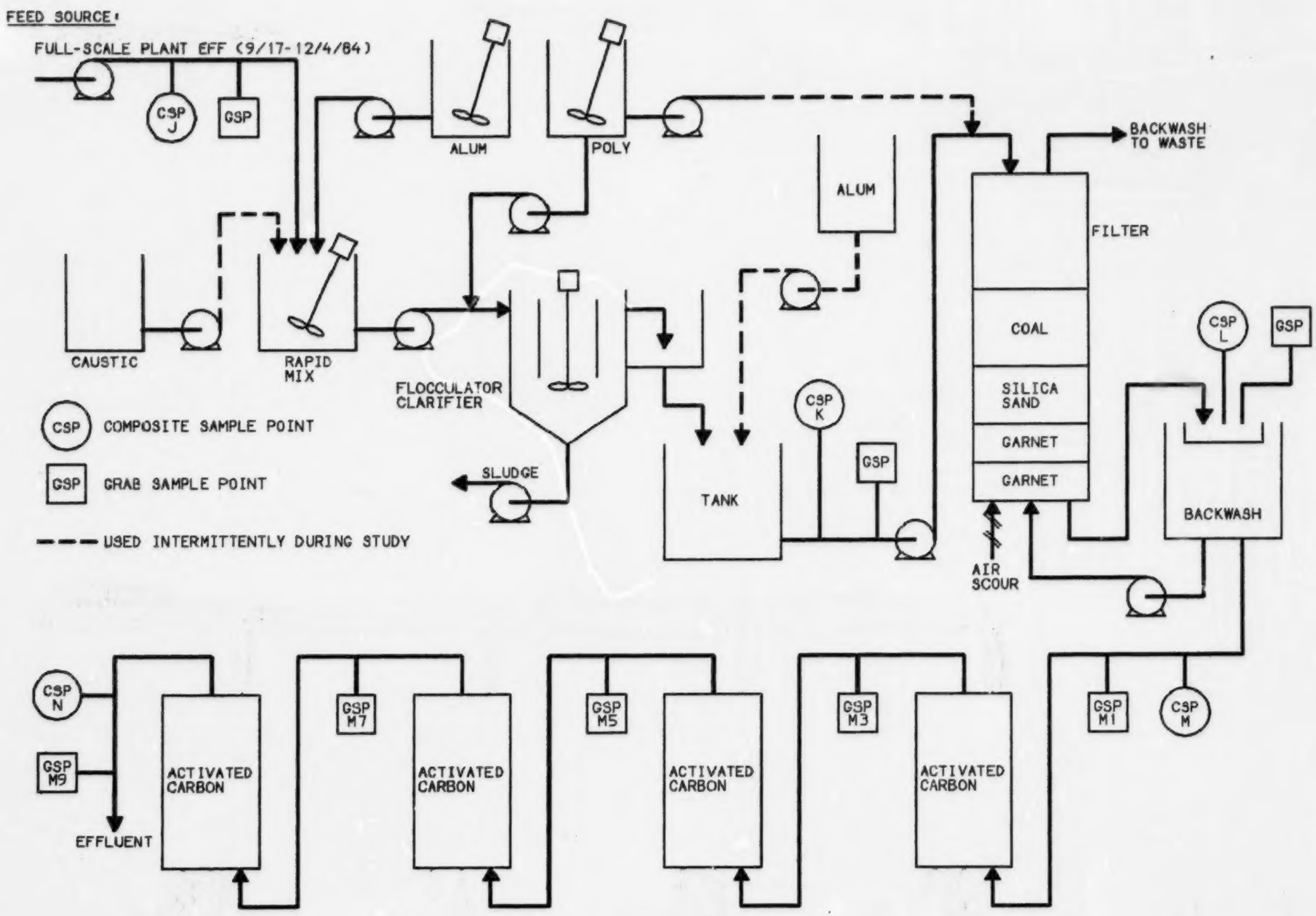

FEED SOURCE:
FULL-SCALE PLANT EFF (9/17-12/4/84)
CSP J
GSP
ALUM
POLY
BACKWASH TO WASTE
ALUM
FILTER
CAUSTIC
RAPID MIX
FLOCCULATOR CLARIFIER
COAL
SILICA SAND
GARNET
GARNET
CSP L
GSP
CSP COMPOSITE SAMPLE POINT
GSP GRAB SAMPLE POINT
USED INTERMITTENTLY DURING STUDY
SLUDGE
TANK
CSP K
GSP
AIR SCOUR
BACKWASH
CSP N
GSP M9
EFFLUENT
ACTIVATED CARBON
GSP M7
ACTIVATED CARBON
GSP M5
ACTIVATED CARBON
GSP M3
ACTIVATED CARBON
GSP M1
CSP M

Figure 11. Physical-Chemical Pilot Plant Schematic Used During GAC Run No. 2 (10/24 to 12/4/84).

carbon was operated in a downflow mode. The second activated carbon run (Figure 11) was made using the upflow mode. This study was performed from 10/24 to 12/4. Note on Figure 11 that the midpoint sampling locations were eliminated from the carbon columns during the second run. A summary of the sampling and analysis schedule for the physical-chemical study is presented in Table 7.

TABLE 7. PHYSICAL-CHEMICAL TREATMENT STUDY - PLANNED SAMPLING AND ANALYSIS SCHEDULE

Location	pH	Turbidity	Temp	TBOD	TSS	TCOD	SCOD	Specific Organics
Clarifier Influent	##	##	##	**	**	**	**	-
MMF Influent	##	##	##	***	***	***	***	-
MMF Effluent	##	##	##	***	***	***	***	-
GAC Influent	##	##	##	-	***	***	***,##	*
GAC-Col #1 Mid[#]	-	-	-	-	-	-	##	-
Col #1 Eff	-	##	-	-	-	-	##	-
Col #2 Mid[#]	-	-	-	-	-	-	##	-
Col #2 Eff	-	##	-	-	-	-	##	-
Col #3 Mid[#]	-	-	-	-	-	-	##	-
Col #3 Eff	-	##	-	-	-	-	##	-
Col #4 Mid[#]	-	-	-	-	-	-	##	-
Col #4 Eff	##	##	##	**	***	***	***,##	*

[*] 12 hour "composite sample" collected manually (grab every 3 hours) four times during study.

[**] 24 hour composite sample collected twice per week. At selected times during the study, TSS and SCOD were run on a daily basis.

[***] Daily 24 hour composite sample.

[#] During GAC Run #2, this sample point was omitted.

[##] Daily grab sample.

NOTE: MMF refers to multi-media filter.

SECTION 7

QUALITY ASSURANCE/QUALITY CONTROL

INTRODUCTION

Sample analyses were conducted on-site in a field laboratory or in the base laboratory in another state. All samples were collected by the pilot plant operators using prelabeled containers.

The on-site laboratory effort included:

1. Providing labeled sampling containers and custody forms;
2. Preserving and shipping samples to the base laboratory;
3. Performing laboratory analyses for TCOD, SCOD, TBOD, NIBOD, NISBOD, chloride, TSS and VSS; and
4. Providing timely data reports from on-site laboratory analyses.

Other project requirements included:

1. Analyzing samples at the base laboratory for total phosphate (TP), ammonia (NH_3), nitrate plus nitrite (NO_2 + NO_3) and total Kjeldahl nitrogen (TKN);
2. Extracting samples for gas chromatography/mass spectroscopy (GC/MS) analyses for specific organics identification; and
3. Preserving and shipping samples using approved methods (5) to other laboratories for further analyses to aid in specific organics identification and interpreting the analytical results.

SAMPLE CUSTODY PROCEDURES

To ensure proper chain-of-custody procedures, labels were prepared for all sample containers and logsheets through a computerized chemical laboratory analysis scheduling system (CLASS). The labeled sample containers and logsheets were provided to pilot plant operators for sample collection on a daily basis to eliminate confusion and inconsistency in sample number assignment.

The CLASS required prefield planning to set up "field groups" to assign sample numbers for storing all analytical results in the CLASS system. The field groups for this project were set up for each station or station group so that trends in the data could be easily observed within each phase.

Logsheet forms were used during the sampling episodes to record sample collection time, date and location at the biological treatment pilot plant and the physical/chemical treatment pilot plant. The on-site laboratory operator provided the logsheet and sample containers daily to pilot plant operators who collected the samples, completed the logsheet and returned both to the on-site laboratory.

CONTAINERS/PREPARATION

Table 8 lists the containers that were used for this project. The 1-gallon and 1-liter plastic cubitainers required no preliminary preparation. The 80 milliliter amber glass bottles were washed with soap and water, rinsed with sulfuric acid and rinsed with deionized water. The 2-liter mason jars for specific organics analyses were washed with hot soapy water; rinsed with hot water, deionized water, acetone and hexane; and then air dried. The same procedure was used to clean the 19-liter glass jars used in the composite samplers while collecting samples for specific organics.

SAMPLING PROCEDURES

Sample Log-In

Sample numbers and logsheet information received from pilot plant operators were reviewed and entered into the computerized data management system. This information appeared on all subsequent data reports.

Sample Preparation

The holding times and preservation techniques associated with analyses performed in the on-site laboratory and at the base laboratory are included in Table 8. Samples for the on-site laboratory were analyzed within 24 hours; therefore, no preservation other than chilling to 4°C was required for TCOD and SCOD analysis.

Samples for NISBOD, SCOD and STOC were filtered on-site through a 0.45 micron filter immediately upon receipt. NISBOD and SCOD analyses were performed at the on-site laboratory. The filtered STOC samples were preserved to pH 2 with H_2SO_4 and chilled to 4°C for shipment to the base laboratory.

Sample Storage and Shipment

All samples were stored in a refrigerator at 4°C until analyses were successfully completed or the sample fraction was shipped in iced coolers to the base laboratory for analysis. Samples were shipped to the base laboratory via air freight approximately once each week.

TABLE 8. CONTAINERS, HOLDING TIMES AND PRESERVATION TECHNIQUES

Parameter*	Minimum Volume for Analysis (ml)	Holding Time (days)	Fraction**	Preservation
Onsite Laboratory Analyses				
TBOD	600	2	C	4°C
NISBOD	600	2	CF	4°C
NIBOD	600	2	C	4°C
TCOD	100	28	S	H_2SO_4, pH 2
SCOD	100	28	SF	H_2SO_4, pH 2
TSS	300	7	C	4°C
VSS	300	7	C	4°C
Cl	300	28	C	4°C
Remote Laboratory Analyses				
TOC	50	28	S	H_2SO_4, pH 2
STOC	50	28	SF	H_2SO_4, pH 2
TKN	1000	28	S	H_2SO_4, pH 2
TP	100	28	S	H_2SO_4, pH 2
NH_3	100	28	S	H_2SO_4, pH 2
$NO_3 + NO_2$	100	28	S	H_2SO_4, pH 2
Specific Organics Extraction	1000	40	W	4°C

* All samples were contained in 1-gallon or 1-liter plastic cubitainers, except samples for TOC and STOC, which were collected and stored in amber-glass bottles and the specific organics samples, which were collected in 2-liter mason jars and stored in Teflon septum vials at 4°C after extraction.

** Fraction codes are:
C = Chilled only, 4°C
CF = Filtered and then chilled, 4°C
S = Preserved with H_2SO_4 to pH 2
W = Organic extractable fraction, 4°C
SF = Filtered and then acidified with H_2SO_4 to pH 2

ANALYTICAL PROCEDURES

General Procedures for Pilot Plant Operators

Analytical procedures used by pilot plant operators are listed below:

1. pH--pH measurements were performed using an Orion pH meter. The pH meter was standardized daily using buffers of pH 4, 7 and 10. Standardization was checked frequently during the day.

2. Temperature--Temperature measurements were made with a laboratory thermometer which had been checked for accuracy against a standard National Bureau of Standards traceable thermometer.

3. Dissolved Oxygen--Dissolved oxygen measurements were made in situ with a Weston & Stack Model 330 dissolved oxygen meter with a Model 61/18 dissolved oxygen probe. This probe has a built-in stirring mechanism to ensure adequate liquid velocity across the membrane. The dissolved oxygen meter was standardized at least once a day using air-saturated tap water. The dissolved oxygen concentration of the tap water was determined chemically using the Azide modification titration method (Method 421B, Standard Methods for the Examination of Water and Wastewater, 15th Ed.). (6)

4. Oxygen Uptake Rates--Oxygen uptake rate measurements were performed on grab samples of mixed liquor obtained immediately before analysis. Mixed liquor samples having a low dissolved oxygen content (less than 4 mg/L) were aerated a short period before testing. Uptake rates were performed on mixed liquor samples in 300 ml BOD bottles using an Orion Model 97-08 dissolved oxygen probe and an Orion 701A pH meter. A Cole-Parmer Model 8385-32 recorder was used to plot the change in dissolved oxygen with time. The straight-line portion of the depletion curve was used to determine the oxygen uptake rate. The probe and meter were standardized immediately prior to performing the oxygen uptake tests by using the procedure described for standardizing the Weston and Stack meter and probe.

5. Turbidity--Turbidity measurements were performed using a Hach Model 2100A turbidimeter. The instrument was standardized frequently using Hach turbidity standards (Cat. No. 12684-00).

Data Quality Objectives for On-site Laboratory and Base Laboratories

The data quality objectives of the analyses are summarized in Table 9. Precision and spike recovery objectives were based on historical laboratory replicate and spike recovery results determined on a variety of natural and wastewater matrices. Actual performance achieved during this study is documented later in this section.

Analytical Procedures and Quality Control (QC) Checks at the On-site Laboratory

Total and Soluble COD--

All samples were analyzed by the Hach colorimetric method (*Federal Register*, Vol. 45, No. 78, April 21, 1980). Chloride levels above 2,000 mg/L will interfere with this method unless samples are diluted or pretreated with mercuric sulfate; therefore, the biological treatment plant

TABLE 9. DATA QUALITY OBJECTIVES

Parameter	Detection Limit (mg/L)	Precision Percent Difference*	Spiking Compound	Recovery*** (%)
TBOD	3**	20	Glucose/Glutamic Acid	100 ± 20
NISBOD	3**	20	Glucose/Glutamic Acid	100 ± 20
NIBOD	3**	20	Glucose/Glutamic Acid	100 ± 20
TCOD	20	15	Potassium Hydrogen Phthalate	100 ± 15
SCOD	20	15	Potassium Hydrogen Phthalate	100 ± 15
TSS	5	15	#	#
VSS	5	20	#	#
Chloride	5	15	Sodium Chloride	100 ± 15
TOC	2	15	Potassium Hydrogen Phthalate	100 ± 15
STOC	2	15	Potassium Hydrogen Phthalate	100 ± 15
TKN	0.10	15	Ammonium Chloride	100 ± 15
Phosphate	0.02	15	Potassium Dihydrogen Phosphate	100 ± 15
NO_3+NO_2	0.009	15	Potassium Nitrate	100 ± 15
NH_3	0.009	15	Ammonium Chloride	100 ± 15

* Percent difference of laboratory duplicates:

$$\% \text{ Difference} = 200 \times \frac{\text{Rep 1} - \text{Rep 2}}{\text{Rep 1} + \text{Rep 2}}$$

** Depends on dilution; 3 mg/L is detection limit (DL) based on no dilution and 40 percent depletion.

*** Percent recovery of spikes in samples:

$$\% \text{ Recovery} = 100 \, \frac{(\text{sample + spike}) - (\text{background of sample})}{\text{true value}}$$

# = Not applicable.

influent was sampled daily the first week and twice each week thereafter for chloride analyses. Based on the results of the chloride analyses, pretreatment with mercuric sulfate was not required for these samples.

Samples for TCOD and SCOD were analyzed daily upon receipt of samples. The minimum QC for TCOD and SCOD included:

1. One blank per day to set 100 percent transmittance,
2. One 500 mg/L reference standard per day to verify Hach curve,
3. Five percent spiked samples per analytical run, and
4. Ten percent replicate samples per analytical run.

TBOD, NISBOD AND NIBOD--

All samples were analyzed by the probe method (EPA Method 405.1, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1979). (7)

Seed check spike analyses for TBOD samples were performed by adding a solution of glucose/glutamic acid to BOD bottles daily to ensure at least 5 percent of the samples were spiked. The viability of the seed material was verified by assuring that measured TBODs for this solution were 200 ± 37 mg/L as specified in Standard Methods. The sample dilution for spiked samples was chosen to allow for depletion caused by the spike to be in the ideal depletion range (i.e., 40 to 70 percent of initial dissolved oxygen) while still conforming to standard methods (at least 2 mg/L depletion of dissolved oxygen with at least 1 mg/L of residual dissolved oxygen remaining in the sample). At least 10 percent of the samples were replicated by setting up one replicate dilution with each analytical run.

TSS and VSS--

All samples for TSS were analyzed by the gravimetric method (EPA Method 160.2). All samples for VSS were analyzed by the gravimetric method (EPA Method 160.4, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1979).

QC for these parameters included setting up a blank crucible and filter with each analytical run. At least 10 percent of the samples were replicated. An internal standard reference weight (Class "S" weight) was used during both tare and final weighings to ensure proper calibration. A minimum of 5 ml of sample was filtered to assure adequate detection limits and data accuracy.

Chloride--

All samples for Cl were analyzed by the titrimetric mercuric nitrate method (EPA Method 325.2). At least 5 percent of the samples were spiked and 10 percent replicated. The titrant was standardized with standard sodium chloride solution.

Analytical Procedures and QC Checks at the Base Laboratory

The following QC checks were applicable for each of the methods used at the base laboratory:

1. At least one blank was analyzed with each lot.
2. At least five calibration standards (where applicable) were analyzed with each daily lot.
3. The correlation coefficient for each standard curve exceeded 0.995.
4. The number of replicates was greater than or equal to 10 percent of the number of samples.
5. The number of spikes was greater than or equal to 5 percent of the number of samples.
6. The difference between replicate concentrations did not exceed the upper control limit (set at three standard deviations above the mean plus the detection limit) for that analysis for this study.
7. The percent recovery of spikes was within the allowed range, which was equal to the three-standard-deviation upper or lower control limit of the QC chart for that analysis for this study.

TOC and STOC--

All samples analyzed for TOC and STOC were analyzed by the wet oxidation method (EPA Method 415.1, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1979). Potential interferences due to the presence of carbonate and bicarbonate carbon were eliminated by acidification and purging of samples prior to combustion.

TKN--

All samples analyzed for TKN were analyzed by the Block digester AAII/semi-automated colorimetric method (EPA Method 351.2, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1979).

TP--

All samples analyzed for TP were analyzed by the colorimetric automated ascorbic acid method (EPA Method 635.1, Methods for Chemical Analysis for Water and Wastes, EPA-600/4-79-020, March 1979).

NH_3--

All samples analyzed for NH_3 were analyzed by the colormetric automated phenate method (EPA Method 350.1, EPA-600/4-79-020, March 1979).

$NO_3 + NO_2$--

All samples analyzed for $NO_3 + NO_2$ were analyzed by the colorimetric, automated cadmium reduction method (EPA Method 353.2, EPA-600/4-79-020, March 1979).

Specific Organics--

Composite samples for specific organic analyses were taken with ISCO samplers fitted with new pump tubing. New Teflon tubing was used to convey samples to and from the sampler. Samples were iced during collection. Procedures for analysis of these samples are described in Section 10.

STATISTICAL EVALUATION OF LABORATORY DUPLICATE ANALYSES

Replicate analyses are summarized in this section for TBOD, NIBOD, NISBOD, TCOD, SCOD, Cl, TOC, STOC, TKN, NH_3, NO_3 + NO_2 and TP. Also, the results of the split samples collected during the Phase 3 intensive testing effort of the biological system for SCOD analyses are discussed in this section.

Presented in Table B-1 in Appendix B are the replicate results. Table 10 summarizes the mean percent difference results for the replicate analyses by parameter. Data from the physical/chemical and biological systems were analyzed on the same day, and the analytical data were entered in the same data batches. Therefore, the QC data reported in the tables are a combination of biological and physical/chemical replicate QC samples.

TABLE 10. SUMMARY OF REPLICATE ANALYSIS

Parameter	Observations	Mean Difference (Percent)	Standard Deviation (Percent)
TBOD	26	5.3	4.2
NIBOD	20	4.9	3.9
NISBOD	21	5.0	5.0
TCOD	87	2.8	4.0
SCOD	136	4.5	6.7
TSS	173	4.9	5.8
VSS	57	5.2	5.6
Cl	32	2.3	2.3
TOC	38	8.0	10.5
STOC	19	7.6	14.5
TKN	13	5.8	5.8
TP	5	2.5	1.4
NO_3+NO_2	12	5.6	8.0
NH_3	13	5.6	8.1

Results

Of 652 replicate samples, 618 (94.8 percent) were within the precision percent difference criteria presented in Table 9 (see Table B-1, Appendix B). Of the 34 samples outside the precision criteria, 2 were for TCOD, 8 for SCOD, 11 for TSS, 3 for volatile MLSS (MLVSS), 5 for TOC, 2 for STOC, 1 for NH_3, 1 for TKN and 1 for $NO_3 + NO_2$. The samples outside the precision criteria were not excluded from the data base.

Split Sample Results

Results of SCOD analyses of the samples split with EPA Hazardous Waste Environmental Research Laboratory (formerly the Industrial Environmental Research Laboratory - IERL) are presented in Table 11 and indicate acceptable analytical precision for samples analyzed by two different laboratories. Precision criteria specified in Table 9 (± 15 percent difference) were met in 9 of the 12 samples. Samples collected on October 13 and 16 at Station F2 differed by 21 percent and the samples collected October 16, 1984, at Station F3 differed by 16.5 percent. Although these values exceed the precision criteria, they are not considered unacceptable in terms of inter-laboratory (two or more laboratories analyzing split samples) precision. EPA has not promulgated an inter-laboratory criterion for SCOD by this method at this time but the criterion is expected to be greater than the intra-laboratory (within one laboratory) criterion due to the increased variability between laboratories.

Factors which may have contributed to the variability of split samples for this project are sample handling, preservative and analytical procedures. On-site laboratory samples were analyzed on the day of collection with no preservative. The same samples split for EPA were

TABLE 11. SUMMARY OF SPLIT SAMPLE RESULTS FOR SCOD MEASURED DURING PHASE 3

	SCOD (mg/L)					
	Station F1		Station F2		Station F3	
Date	Base Lab	HWERL*	Base Lab	HWERL*	Base Lab	HWERL*
10/13/84	424	456	216	268	811	719
10/16/84	476	463	218	271	919	779
10/21/84	448	434	231	243	796	722
10/24/84	419	424	180	204	684	658

*Hazardous Waste Environmental Research Laboratory preserved with concentrated sulfuric acid to a pH of less than two and were analyzed several days later.

STATISTICAL EVALUATION OF LABORATORY ANALYTICAL ACCURACY

Accuracy checks pertinent to the parameters analyzed during the study are summarized in this section for TBOD, NIBOD, NISBOD, TCOD, SCOD, Cl, TOC, STOC, TKN, NH_3, $NO_3 + NO_2$ and TP analyses.

Spike analyses were not applicable and therefore not performed for TSS and VSS analyses. Accuracy for these parameters was controlled by calibration prior to using balance, checks for proper calibration after reading crucibles and analysis of blank crucibles in the analytical scheme.

Presented in Table B-2 in Appendix B are the results of spike analyses. Table 12 summarizes the spike recovery data. During the analyses and reporting of the data, physical/chemical and biological systems' data were analyzed in the same day so the data were entered on the same data batches. Therefore, the QC data reported in the tables are a combination of biological and physical/chemical spiked QC samples.

TABLE 12. SUMMARY OF SPIKE RECOVERY DATA OBTAINED DURING STUDY

Parameter	Observations	Mean (Percent)	Standard Deviation (Percent)
TBOD	80	93.5	9.0
NIBOD	21	89.7	9.3
NISBOD	20	86.6	9.7
TCOD	83	96.2	4.4
SCOD	93	96.8	4.8
TSS	*	*	*
VSS	*	*	*
Cl	30	98.5	3.8
TOC	22	101.4	12.9
STOC	13	107.3	9.3
TKN	9	105.1	17.0
TP	4	99.0	3.9
NO_3+NO_2	10	95.7	7.9
NH_3	10	98.3	4.9

* Not applicable.

Results

Of 322 spike samples, 303 (94.1 percent) were within the percent recovery criteria presented in Table 9 (see Table B-2, Appendix B, Reporting Period 1). For the 19 sample spikes outside the percent recovery criteria, 4 were for TOC, 2 for STOC, 4 for TBOD, 2 for NIBOD, 3 for NISBOD, 3 for TKN and 1 for NO_3+NO_2. The samples outside the percent recovery criteria were not excluded from the data base.

Mean recoveries of the glucose/glutamic acid seed checks analyzed during the study had lower mean recoveries and a larger standard deviation compared to spiked samples measured for glucose/glutamic acid additions. Seed spike checks for the study had a mean recovery plus or minus one standard deviation of 82 ± 16 percent. The secondary check for seed viability (spikes into seeded samples) yielded results that were within criteria for all but three cases when the primary check failed. These results suggest adequate seeding protocol. Samples analyzed for TBOD and NIBOD did not require biological seed additions (as defined in the analytical protocol). Spikes were performed for these analyses to verify the validity of not seeding.

Mean spike recoveries for all parameters were good, with means within 100 ± 10 percent during the study except for NIBOD and NISBOD (see Table 12).

Quality Assurance (QA) Audit Results

The project QA Supervisor introduced a performance sample for TBOD and TCOD into the analytical system. The true value was withheld from the analyst and the sample was treated the same manner as normal samples. The following results were reported to the QA supervisor, who informed the analyst that both values were acceptable:

Parameter	Reported Value	Certified Value	Target Range
TBOD (mg/L)	35	37	25-49
TCOD (mg/L)	53	61	46-76

PERCENT COMPLETION/PERCENT DELETION RESULTS

As shown in Table 13, 98.1 percent of the total analyses requested were completed. Analyses for four parameters (TOC, STOC, TKN and TP) were less than 95 percent complete due to:

1. Sample container breakage during shipment to the base laboratory (TOC, STOC);
2. Sample spillage (TKN); and

3. The cancellation of Phase 5 testing (TKN, TP).

Also shown in Table 13, 1.5 percent of the analytical results were deleted due to suspected incorrect sample identification or analytical technique.

TABLE 13. PERCENT COMPLETION/PERCENT DELETION RESULTS

Parameter	No of Analyses Requested	No. of Analyses Performed	Percent Complete (%)	No. of Analyses Deleted Due to Suspect Data	Percent Deleted (%)
TBOD	224	216	96.4	2	0.9
NIBOD	66	63	95.5	1	1.5
NISBOD	62	59	95.2	2	3.4
TCOD	674	666	98.8	13	2.0
SCOD	950	948	99.8	12	1.3
TSS	1,099	1,095	99.6	6	0.5
VSS	266	265	99.6	3	1.1
Cl	39	38	97.4	0	0
TOC	243	221	90.9*	12	5.4
STOC	111	95	85.6*	6	6.3
TKN	24	21	87.5**	0	0
TP	10	9	90.0**	0	0
NH_3	18	18	100.0	0	0
NO_3 + NO2	18	18	100.0	0	0
TOTAL	3,804	3,732	98.1	57	1.5

* Less than 95 percent complete due to sample container breakage during shipment to the base laboratory.

** Less than 95 percent complete due to sample spillage and miscommunication of analyses needed after cancellation of Phase 5 testing.

SECTION 8

BIOLOGICAL PROJECT RESULTS

INTRODUCTION

The effect of powdered activated carbon (PAC) on the biological treatment of pharmaceutical wastewater was studied using three biological pilot plants. One unit was used as a control unit and the other two units were operated with different doses of PAC added to the influent end of the aeration tank. Operational parameters were similar to those used by the full scale plant at the start of the tests. Prior to the start of the pilot testing, a grab sample of raw wastewater was analyzed to evaluate the need for nutrient addition and to determine the current wastewater characteristics. The results of these analyses, a description of the full scale plant raw and effluent characteristics during the course of the biological testing and the results of the biological pilot plant tests are presented in this section.

The biological pilot plants were operated from September 7, 1984 to November 29, 1984. An extensive program of sampling and analysis was performed during this time. All analytical results and operational measurements are presented in Appendix A, Table A-1 and Appendix C. Significant results and selected summaries are presented in this section. In most cases, the data discussion is based on the test plan phases presented in the Biological Test Plan part of Section 6.

Operational problems resulted in the cancellation of the second intensive testing period (Phase 5 of the Test Plan). Two periods of relatively stable performance before the onset of the operational problems were substituted for Phase 5 to characterize the performance of the PAC biological units.

BENCH TEST RESULTS

Grab samples of raw wastewater and mixed liquor were obtained on July 26, 1984 for analyses to aid in the planning of the pilot plant operation. The purpose of these analyses was to evaluate the need for nutrient addition and confirm influent values of selected parameters used in control of the activated sludge process.

The results of the analyses are shown in Table 14. Based upon these results it appeared that the concentrations of nitrogen (assuming organic nitrogen is available) and phosphate in the raw wastewater were high enough so that nutrient addition would not be required. The low pH of this grab sample indicated that the pH of the biological treatment units should be closely watched during the pilot plant operation. The mixed liquor suspended solids concentration was 4,000 mg/L.

CONVENTIONAL BIOLOGICAL TREATMENT PERFORMANCE - FULL SCALE PLANT AND BTS-3

Daily 24 hour composite samples of raw wastewater (Sample point B) and full-scale plant effluent (Sample point J) were obtained throughout the pilot test period. Results of the analysis of these samples are presented in Appendix C, Tables C-1, C-2 and C-3. Mixed liquor suspended solids concentrations of the plant aeration tank contents measured by the plant operators are listed in Appendix C, Table C-4. Summaries of the average values and range of values are listed in Tables 15 and 16. The data are grouped into several time periods corresponding to the various test phases

TABLE 14. ANALYTICAL RESULTS OF JULY 26, 1984 SAMPLES FROM FULL-SCALE PLANT

Parameter*	Raw Waste	Mixed Liquor
SBOD, mg/L	1060	**
NISBOD, mg/L	955	**
TCOD, mg/L	3000	**
SCOD, mg/L	2490	**
TOC, mg/L	950	**
STOC, mg/L	690	**
Chloride, mg/L	160	**
TKN, mg/L N	114	**
NH_3 N, mg/L N	18.5	**
Total Phosphate, mg/L P	28.4	**
Soluble Phosphate, mg/L P	24.4	**
pH, units	4.3	**
TSS, mg/L	**	4000
VSS, mg/L	**	3750

* Soluble fractions were determined on filtrate from filtration through Gelman type A-E filter.

** Analysis was not performed.

TABLE 15. SUMMARY OF FULL-SCALE BIOLOGICAL TREATMENT PLANT DATA (GENERAL CHARACTERISTICS)

Phase		Raw Waste (B)					Plant Effluent (J)			Mixed Liquor
		pH	Temp* (°C)	TSS (mg/L)	VSS (mg/L)	Cl (mg/L)	pH	Temp* (°C)	TSS (mg/L)	TSS (mg/L)
Phase 1	Average	**	28	668	471	1400	**	37	775	4080
Start-up	High	10.4	31	1300	630	1700	7.8	40	1560	4600
Day 1-10	Low	8.4	25	325	235	1100	7.7	34	72	3460
	n	10	8	10	10	10	9	7	9	27
Phase 2	Average	**	28	705	511	1420	**	25	215	4290
Acclimation	High	11.5	32	1320	800	1630	8.6	29	600	5330
Day 11-33	Low	9.7	23	360	240	1130	7.6	21	65	2960
	n	23	23	23	10	7	15	15	15	69
Phase 3	Average	**	26	709	488	1230	**	27	330	4210
Intensive Test	High	12.0	***	1180	720	1450	8.6	27.5	593	4970
Day 34-47	Low	7.3	***	370	240	1000	8.0	26	248	3690
	n	14	1	14	14	6	14	2	14	39
Phase 4	Average	**	***	562	402	1050	**	21	280	3970
Acclimation	High	11.4	***	1300	590	1470	8.6	30.5	580	5640
& Tests	low	6.5	***	200	140	339	7.8	14	130	2960
Day 48-84	n	36	***	36	18	12	38	30	38	83
Phases 1-4	Average	**	28	639	460	1260	**	24	337	4120
Entire Test	High	12.0	32	1320	800	1700	8.6	40	1560	5640
Period	Low	6.5	23	200	140	339	7.6	14	65	2960
Day 1-84	n	83	32	83	52	35	76	54	76	218

*Temperature measured on grab samples. Other measurements performed on composite samples.

**Average values not calculated for pH.

***Raw waste temperature not measured after Day 34.

TABLE 16. SUMMARY OF FULL-SCALE BIOLOGICAL TREATMENT PLANT DATA (ORGANICS)

Phase		Raw Waste (B)			Plant Effluent (J)			Removals	
		TCOD (mg/L)	TBOD (mg/L)	TOC (mg/L)	TCOD (mg/L)	SCOD (mg/L)	TBOD (mg/L)	TCOD (%)	TBOD (%)
Phase 1	Average	7830	3020	1980	1810	*	117	77	98
Start-up	High	8870	3500	2250	3180	*	160	88	*
Day 1-10	Low	6130	2500	1710	776	*	74	62	*
	n	10	4	9	9	*	2	9	1
Phase 2	Average	7300	2860	2070	1010	*	76	86	97
Acclimation	High	12000	4100	2380	1360	*	110	90	98
Day 11-33	Low	5350	2000	1380	794	*	63	74	97
	n	23	5	8	15	*	10	15	4
Phase 3	Average	8120	2700	1900	1500	871	136	81	94
Intensive Test	High	12000	3900	2610	2160	1130	200	88	97
Day 34-47	Low	5510	1900	1560	1260	701	99	74	91
	n	14	5	14	12	14	5	12	4
Phase 4	Average	6250	2600	1810	1440	812	174	73	93
Acclimation	High	9290	3000	2830	2580	1330	340	90	97
& Tests	Low	2260	1700	1310	730	412	66	50	90
Day 48-84	n	35	8	9	17	36	12	15	7
Phase 1-4	Average	7060	2760	1930	1400	829	130	79	95
Entire Test	High	12000	4100	2830	3180	1330	340	90	98
Period	Low	2260	1700	1310	730	412	63	50	90
Day 1-84	n	82	22	40	53	50	29	51	16

* Analysis not performed.

of the biological pilot plant operations. The data in the summary tables show that the raw wastewater pH and TCOD varied over a wide range during the entire test period. The range of variation in TBOD and TOC was not as great as for TCOD. In spite of the great variability in influent TCOD and pH, effluent TCOD and pH values were much less variable. The variations in parameter values can best be illustrated by data plots. Figure 12 shows the variation in influent and effluent TCOD. Removals of TCOD and TBOD by the full-scale biological plant are shown on Figure 13. Measured TBOD removals were better than 90 percent and were relatively consistent. TCOD removals were much less consistent. Although the poor TCOD removals on Days 5 and 9 can be attributed to high effluent suspended solids, the low percent removal during the period from Days 56 to 60 can be partly attributed to low influent TCOD levels with little change in effluent TCOD. Figure 14 graphically shows that TCOD values were generally higher when effluent suspended solids were high.

The variation in raw wastewater and effluent pH for the daily composite samples is shown on Figure 15. Although the influent daily composite pH varied from 6.5 to 12, effluent daily composite pH values varied only from 7.6 to 8.6. Caustic was added as needed to the influent to provide sufficient alkalinity to offset nitrification requirements of the pilot plants. Actual influent waste pH values varied over a much wider range than indicated by the daily composite samples. At times, problems with the acid or caustic addition in the neutralization tank resulted in raw wastewater pH values as low as 1.2 (Day 46, October 22, 1984) for a short time.

The average TCOD for 51 daily composite samples of full-scale plant effluent analyzed during the project was 1400 mg/L. The average percent removal of TCOD for these samples was 80 percent, well above the 74 percent BPT removal limit. On 9 of the 51 days, however, the removal was less than 74 percent. Some of the low TCOD removals can be attributed to abnormally high effluent suspended solids (2 days) and to a decrease in influent TCOD concentration while effluent TCOD values remained at normal levels (4 days). Daily composite samples of raw wastewater were analyzed for nutrients near the start and near the end of the pilot testing to evaluate the nutrient balance. Results of these analyses are listed in Table 17. A TBOD:N:P balance of 100:5:1 is considered to be sufficient for the activated sludge process. Most of the nitrogen values were greater than 5 and the phosphate values were greater than 1 in the ratio.

A summary of the effluent characteristics of the experimental control unit (BTS-3) is listed in Table 18. The mixed liquor in this unit settled poorly at the start of the project. By Day 9, the clarifier was full of solids resulting in some sludge being lost over the effluent weir. A second clarifier was installed in parallel on Day 13 and the effluent suspended solids improved. Routine scraping of the sloping sides of the clarifiers to reduce the effect of bridging of the settled solids was started on Day 33. Settling improved so much that the second clarifier was removed from the system on Day 37. A single clarifier, scraped three times per day, performed well for the remainder of the tests.

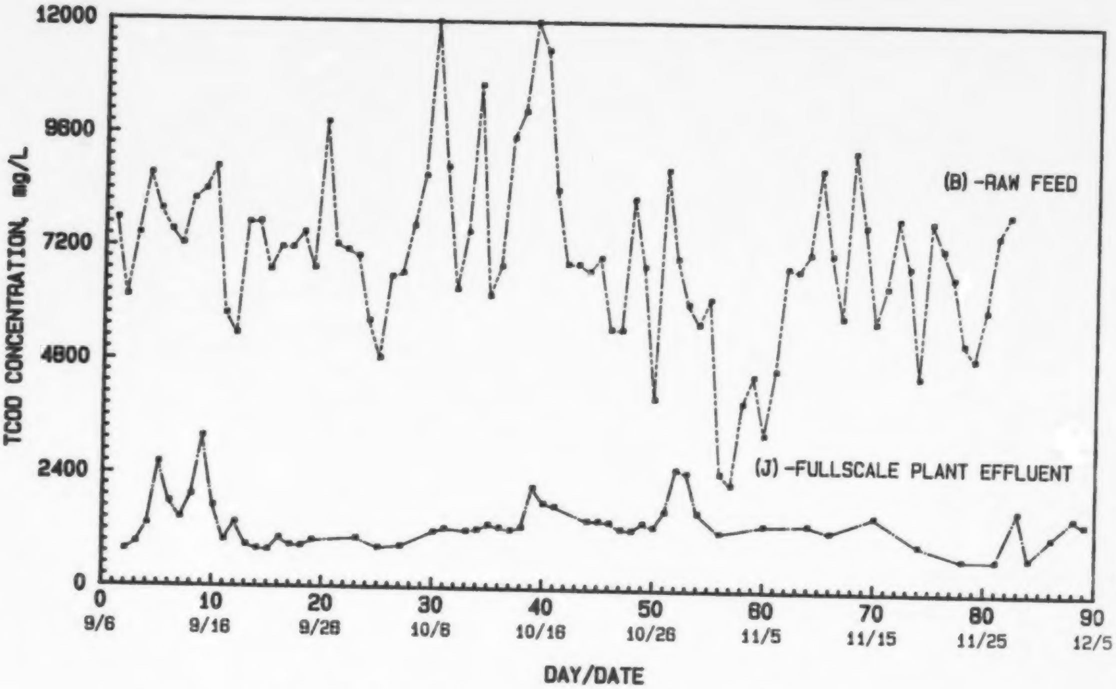


Figure 12. Full-Scale Plant Influent and Effluent TCOD.

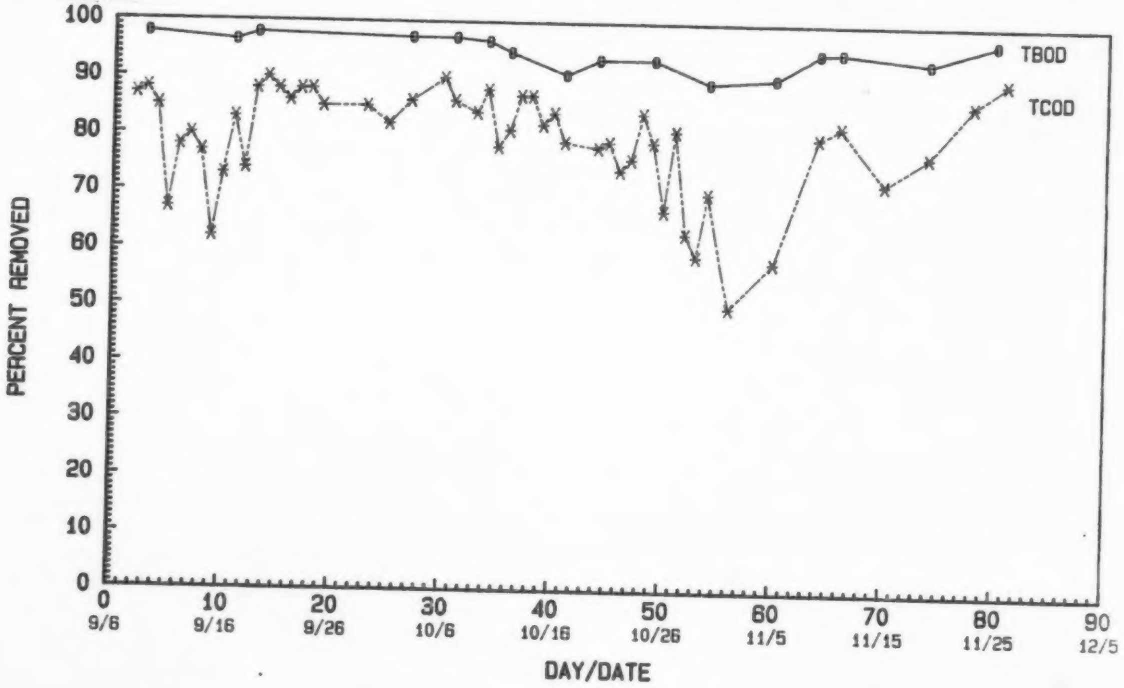


Figure 13. Full-Scale Plant TCOD and TBOD Removals.

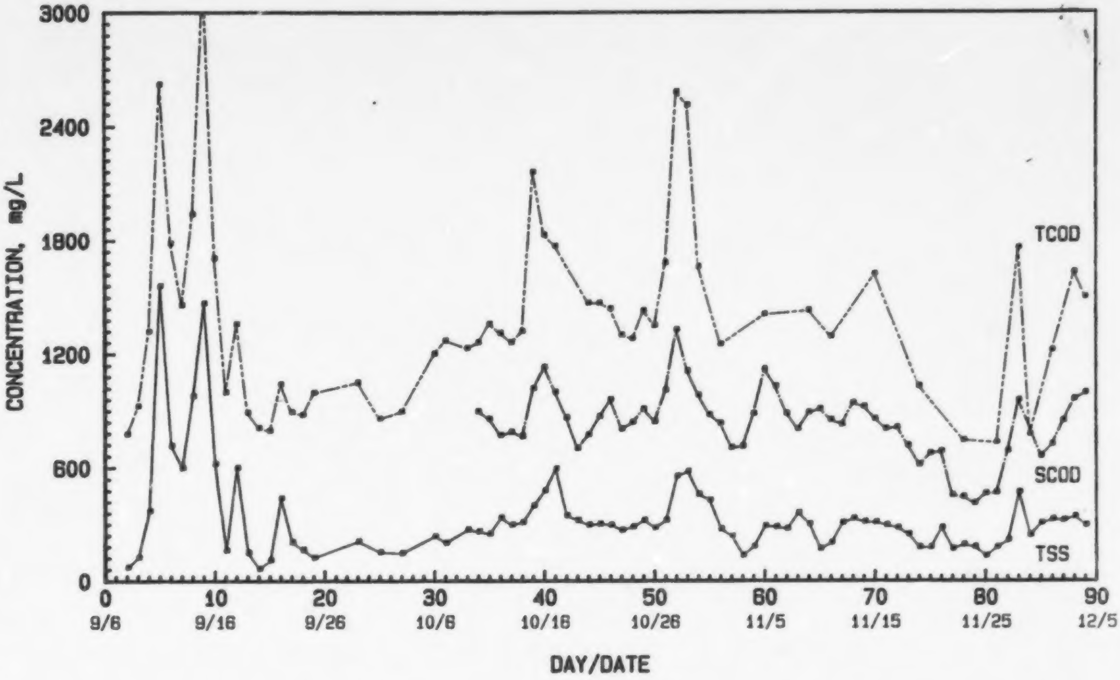


Figure 14. Full-Scale Plant Effluent - TCOD and TSS.

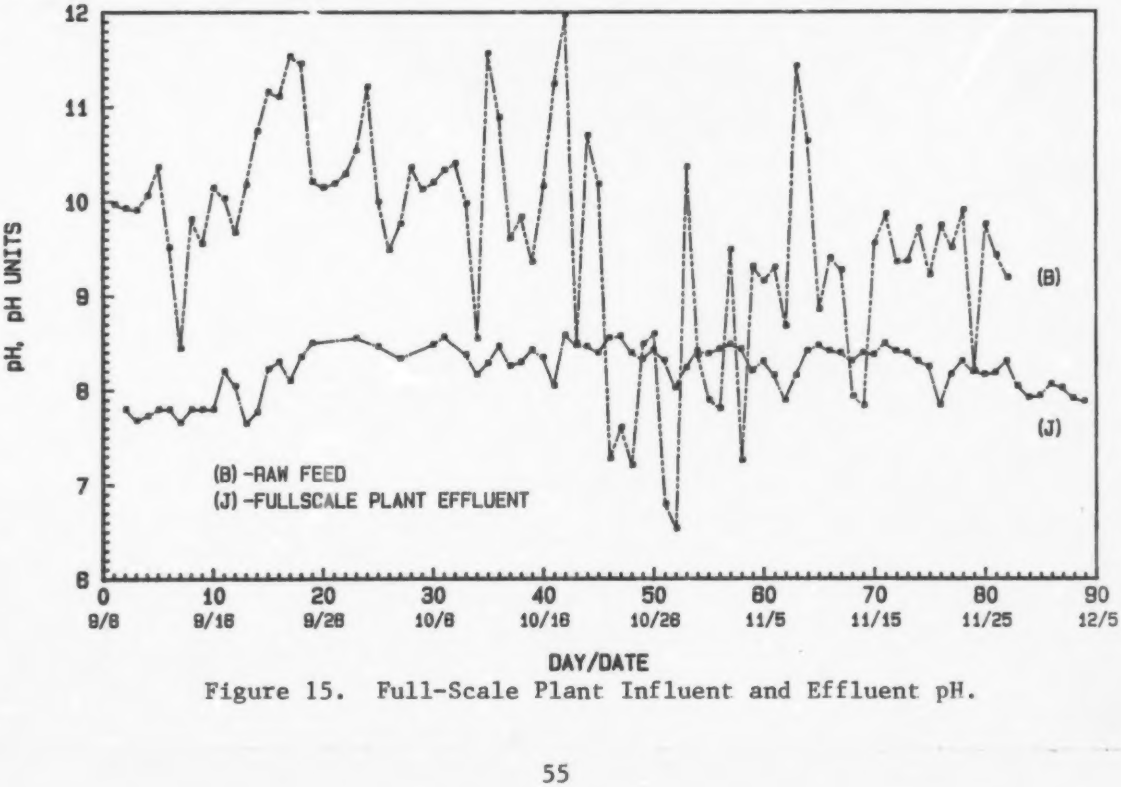


Figure 15. Full-Scale Plant Influent and Effluent pH.

The mixed liquor temperatures of BTS-1 and BTS-2 were significantly higher than that of BTS-3 in the early part of the tests. The air added to the BTS-1 and BTS-2 aeration tanks was pressurized by mechanical blowers located near each aeration tank. The high temperature of the pressurized air (140 to 150°F) contributed to the high BTS-1 and BTS-2 mixed liquor temperatures. BTS-3 mixed liquor, however, was aerated using compressed air from the full-scale treatment plant at ambient temperature. Heaters were installed in the aeration tank cells of BTS-3 on Day 27 to raise the BTS-3 mixed liquor temperature to the BTS-1 and BTS-2 levels.

The effects of changes in the operation of the BTS-3 clarifier on effluent suspended solids and TCOD are shown on Figure 16. High effluent TCOD values were usually associated with high suspended solids concentrations. Figure 17 shows BTS-3 TCOD removal during the pilot plant test period. Daily TCOD removal averaged 84 percent for the entire test period. Only 5 of the 78 daily TCOD removals were less than the BPT monthly average removal of 74 percent.

TABLE 17. FULL-SCALE BIOLOGICAL TREATMENT PLANT NUTRIENT DATA

	Raw Wastewater			
Date	TBOD (mg/L)	TKN (mg/L N)	Phosphate (mg/L P)	TBOD:N:P**
09/07/84	3400	190	25.5	100: 5.6:0.8
09/08/84	*	380	36.9	***
09/09/84	3500	450	48	100:12.8:1.4
09/10/84	*	450	53	***
09/11/84	2700	385	43.8	100:14.2:1.6
09/12/84	*	350	31	***
09/13/84	2500	400	43.5	100:16 :1.7
09/15/84	*	350	45.6	***
11/15/84	*	250	*	***
11/19/84	1700	65	*	100: 3.8:-*
11/25/84	2300	380	*	100:16.5:-*
11/27/84	3500	410	*	100:11.7:-*

* Analyses not performed.

** Minimum of 5 for N and 1 for P in ratio generally regarded as necessary for aerobic biological treatment

*** Calculation not performed.

TABLE 18. SUMMARY OF BTS-3 EFFLUENT ANALYTICAL DATA

Phase		pH	TCOD (mg/L)	SCOD (mg/L)	NIBOD (mg/L)	NISBOD (mg/L)	TOC (mg/L)	STOC (mg/L)	TSS (mg/L)	VSS (mg/L)
Phase 1	Average	*	1150	848	>62**	>16**	320	259	215	190
Start-up	High	8.3	1640	913	>84	>36	370	283	580	440
Day 1-10	Low	8.0	833	776	44	9	244	232	51	80
	n	8	9	8	2	2	4	3	9	8
Phase 2	Average	*	1320	951	120	22	338	258	250	256
Acclimation	High	8.7	2590	1060	252	28	443	298	1460	1250
Day 11-33	Low	8.0	929	824	42	14	287	227	38	35
	n	23	20	20	4	4	9	10	22	10
Phase 3	Average	*	1070	825	27	<8	290	223	143	109
Intensive	High	8.1	1190	929	38	16	363	253	273	227
Tests	Low	6.4	894	684	16	5	265	194	89	55
Day 34-47	n	14	14	14	6	5	14	14	14	14
Phase 4	Average	*	792	650	18	8.7**	253	217	108	98
Acclimation	High	7.9	1300	759	27	15	264	241	590	485
and Tests	Low	6.4	578	492	10	4	220	192	23	40
Day 48-84	n	36	36	36	8	6	7	8	36	18
Phases 1-4	Average	*	1020	779	46**	13**	299	234	165	147
Entire Test	High	8.7	2590	1060	252	>36	443	298	1460	1250
Period	Low	6.4	578	492	10	4	220	192	23	35
Day 1-84	n	81	79	78	20	17	34	35	81	50

*Average values not calculated for pH.

**Average values do not include data reported as "less than" (<) or "more than" (>) analytical method limits.

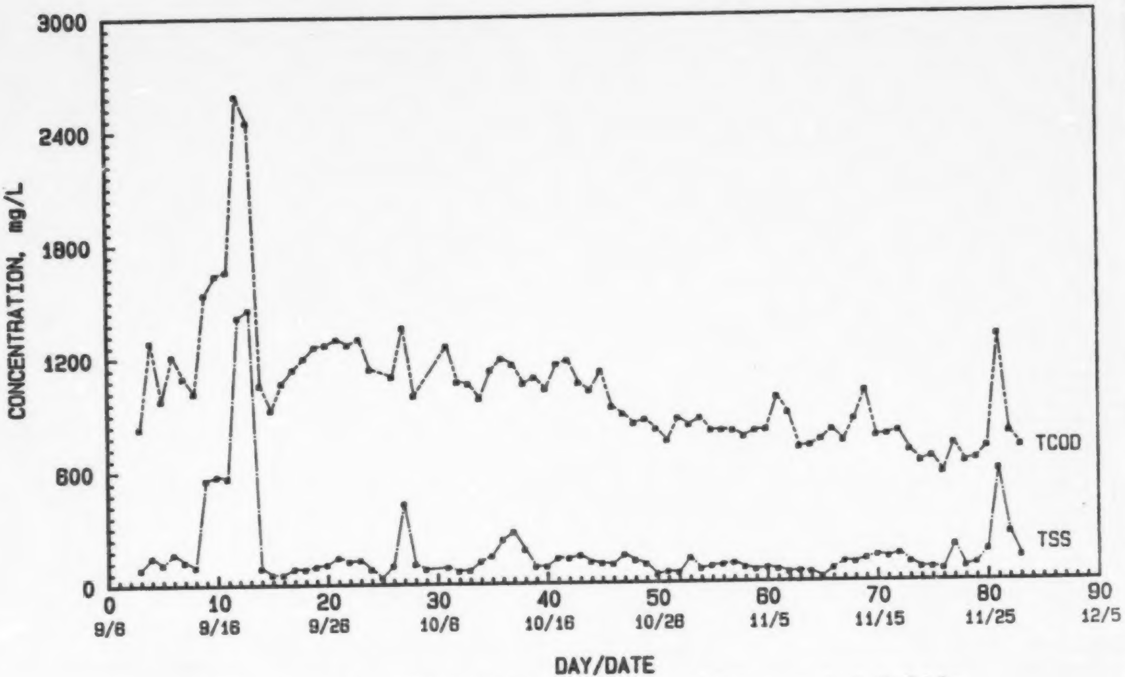


Figure 16. BTS-3 Effluent TCOD and Suspended Solids.

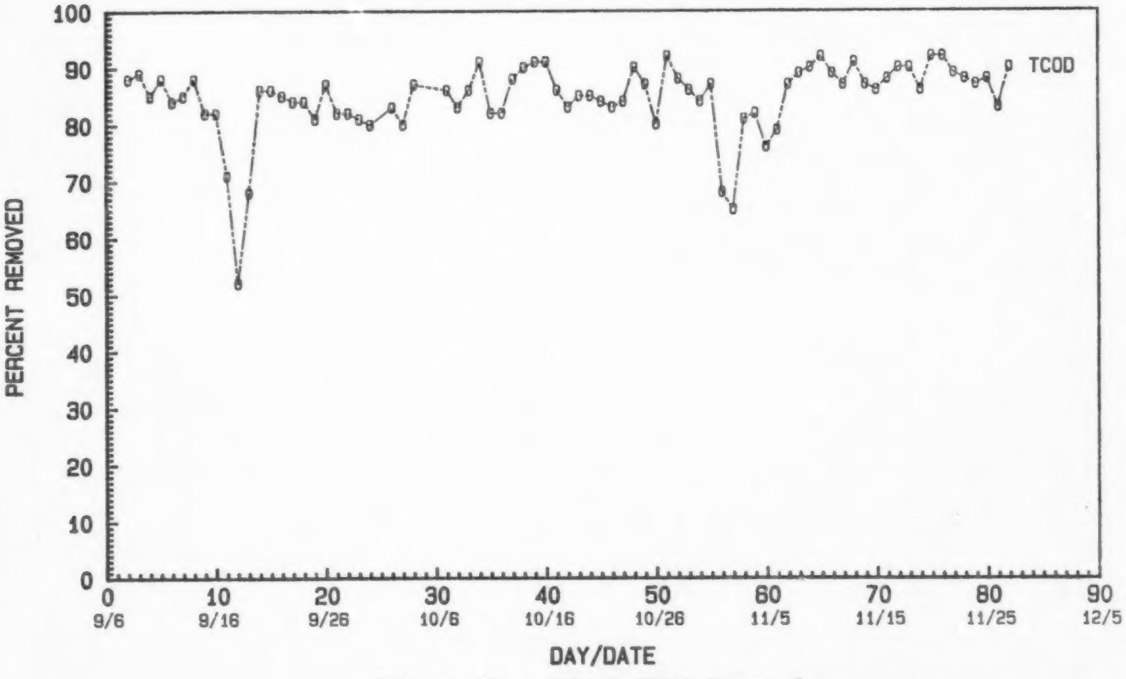


Figure 17. BTS-3 TCOD Removal.

Figures 18 and 19 compare the daily average values for TCOD and SCOD for the full-scale effluent and BTS-3 effluent. Although the full-scale plant effluent TCOD was generally higher than the BTS-3 effluent, the SCOD values were similar.

PHASE 1 - START-UP PERIOD

All three pilot units were filled with mixed liquor from the full-scale plant aeration tanks on September 7, 1984. Aeration was started immediately followed by the addition of raw wastewater. Wasting of mixed liquor was started the following day. The feed raw waste composite sampler (sample point B) was started on September 8 and the effluent composite samplers (sample points F1, F2 and F3) were started on September 9, 1984. September 7 was designated as "Day 1" of operation.

The three biological treatment pilot plants were operated for ten days after start-up before powdered activated carbon was added to BTS-1 and BTS-2. Operating parameters were adjusted to the desired levels and the performance of the three pilot units operating under similar conditions was compared.

BTS-1 and BTS-2 operated with few problems during this phase. Because the BTS-3 clarifier was not being routinely scraped, it began filling with sludge and solids were going over the clarifier weir by Day 9, resulting in increased concentrations of TCOD and suspended solids in the effluent. The influent and effluent TCOD values for this phase are shown on Figure 20. Effluent suspended solids values are shown on Figure 21. SCOD levels in the effluents are shown on Figure 22. In spite of the high suspended solids content of BTS-3 effluent on Days 9 and 10, the SCOD was little changed. Mixed liquor suspended solids values are shown on Figure 23. Although the BTS-3 mixed liquor suspended solids were somewhat lower than for BTS-1 and BTS-2 in this part of the phase, the differences narrowed at the end of the phase. The food to microorganism (F/M) ratios in terms of grams of TCOD added per day per gram of mixed liquor suspended solids are shown on Figure 24 for BTS-3.

A summary of operational and analytical data for the last four days of the start-up phase is presented in Table 19. This period represented a relatively stable period of operation approximately two hydraulic retention times after start-up and immediately before PAC addition to BTS-1 and BTS-2 was started. Data from this period can be used to compare the performance of the three pilot plant units when operated in a similar manner. Operational parameters were similar for all units with the exception of temperature and return sludge (RS) flow. The temperature of the mixed liquor in BTS-1 and BTS-2 was higher than BTS-3 because of the higher temperature of the air used for aeration. The BTS-3 return sludge flow was kept at a high level in an effort to remedy solids settling problems in the clarifier. Sludge volume index (SVI) values were the same for all three mixed liquor samples but without routine scraping of the clarifier, the sludge completely filled the clarifier. Effluent quality parameters were similar for all three units with the exception of high effluent suspended

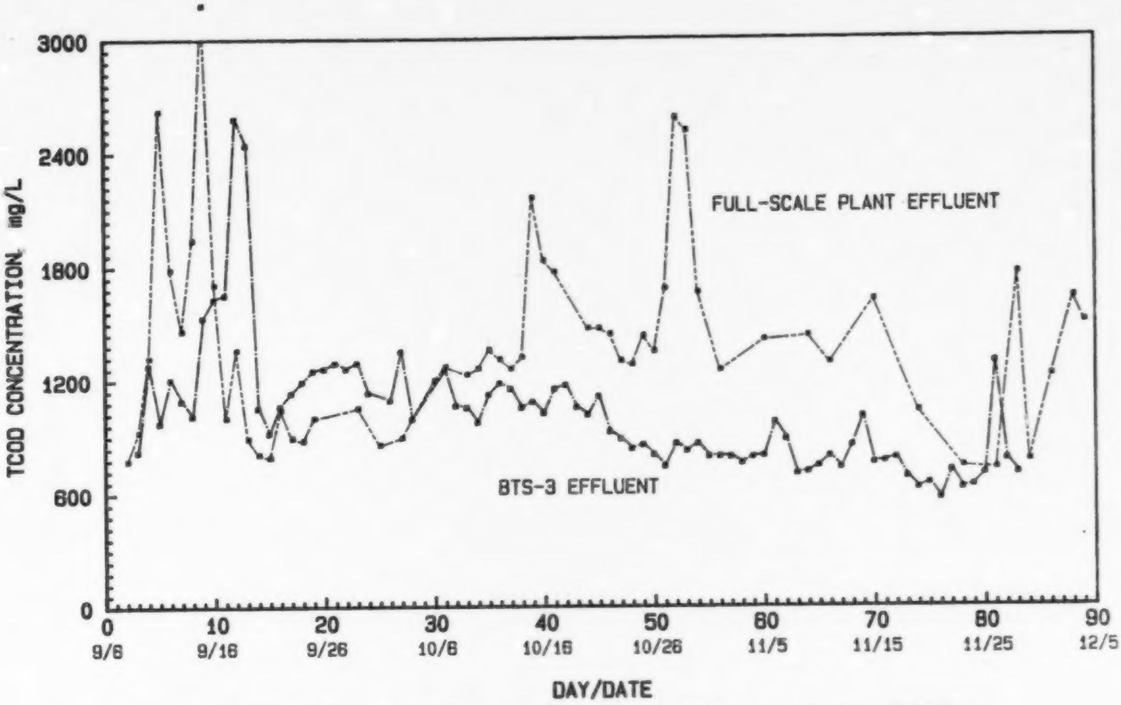


Figure 18. Full-Scale Plant and BTS-3 Effluent TCOD.

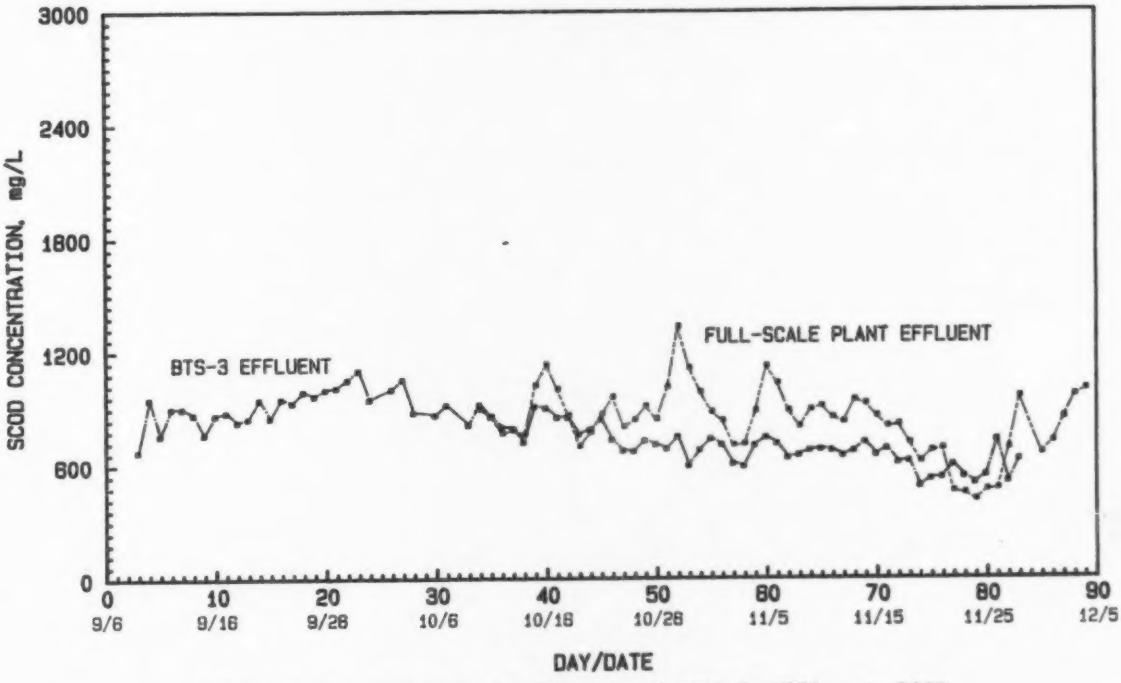


Figure 19. Full-Scale Plant and BTS-3 Effluent SCOD.

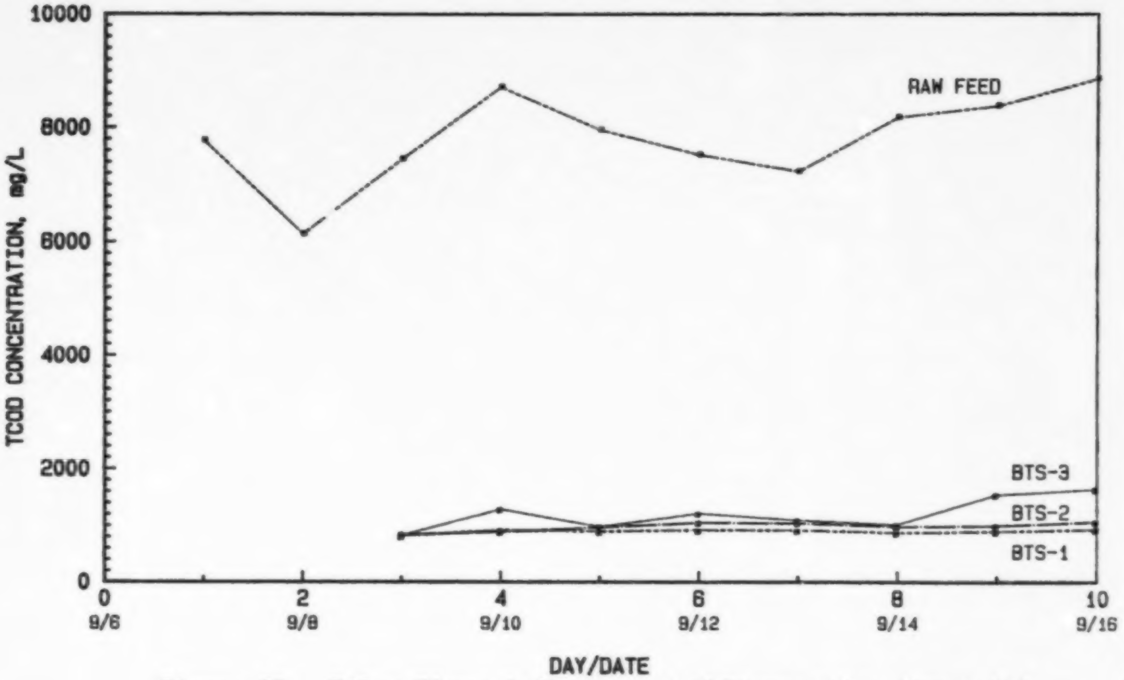


Figure 20. Pilot Plant Influent and Effluent TCOD (Day 1-10).

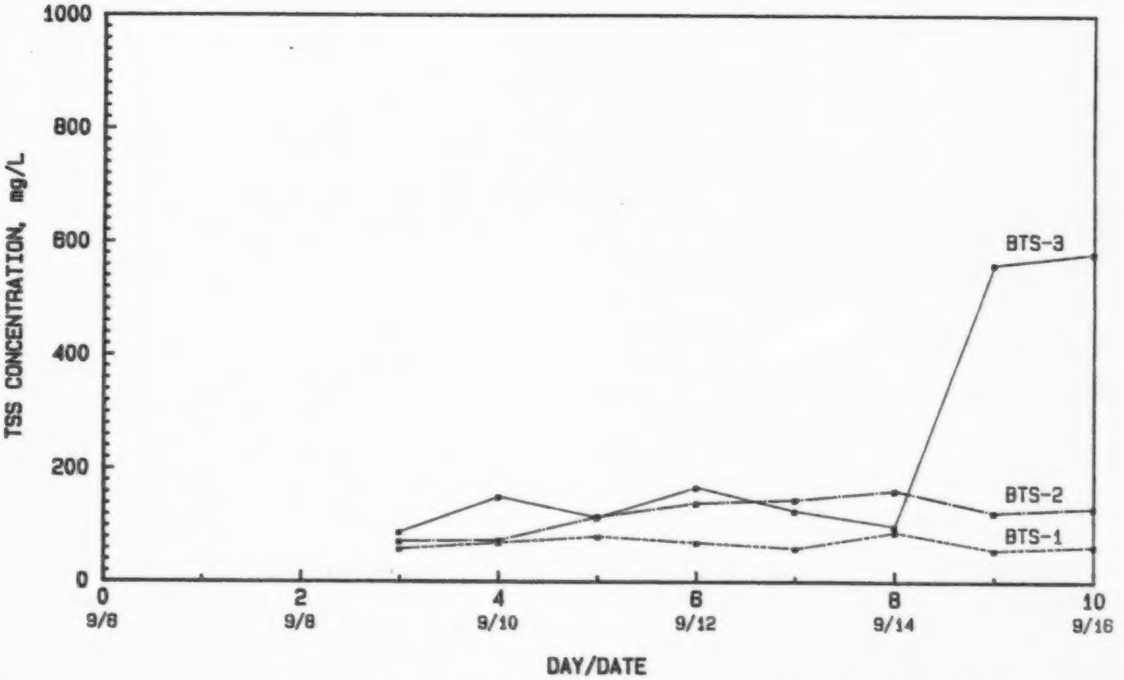


Figure 21. Pilot Plant Effluent Suspended Solids (Day 1-10).

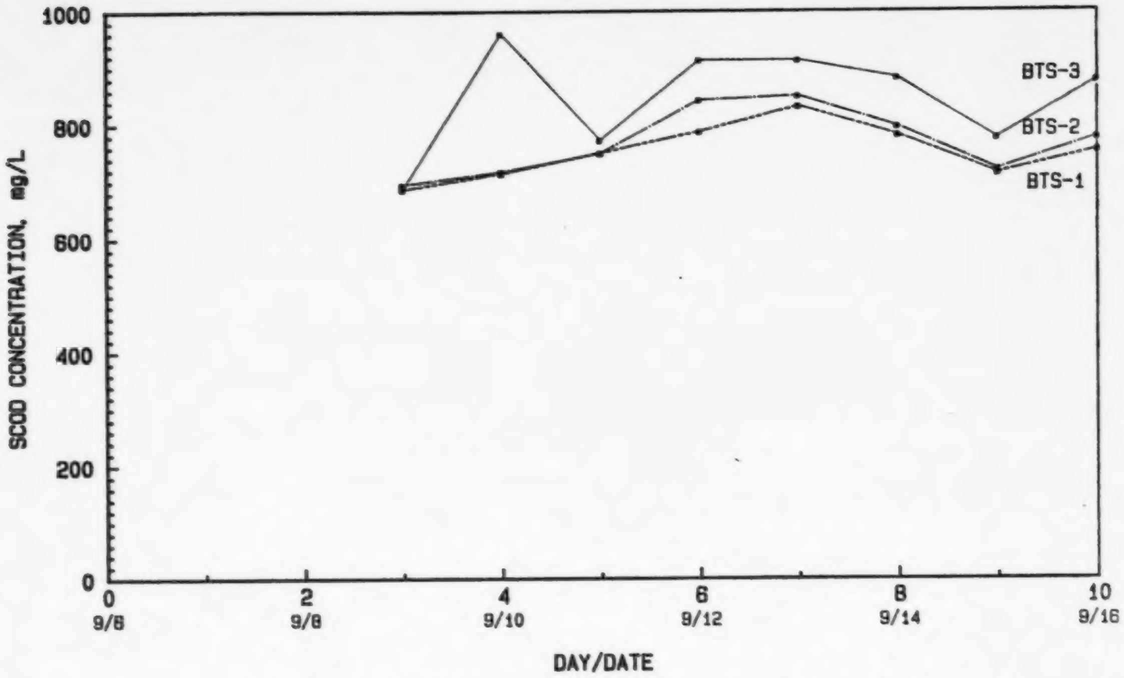


Figure 22. Pilot Plant Effluent SCOD (Day 1-10).

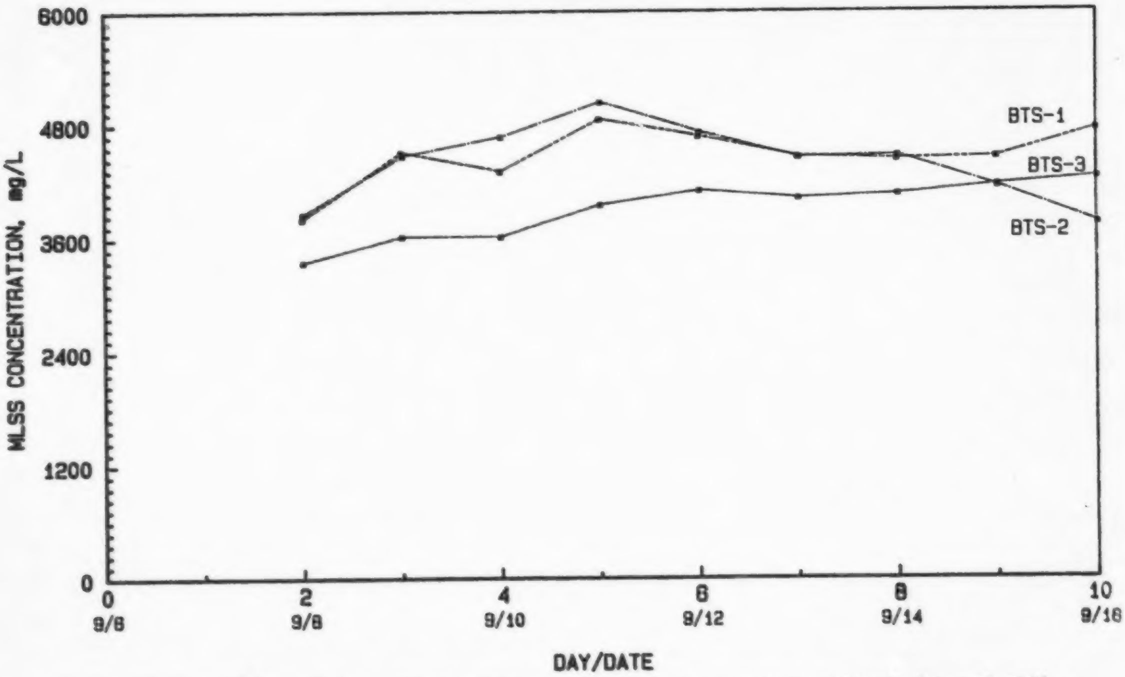


Figure 23. Pilot Plant Mixed Liquor Suspended Solids (Day 1-10).

TABLE 19. SUMMARY OF BIOLOGICAL PILOT PLANT OPERATION AT END OF START UP PERIOD (SEPTEMBER 13-16, 1984)

Parameter	BTS-1		BTS-2		BTS-3	
	Average (n)	Range	Average (n)	Range	Average (n)	Range
Operational Data						
Feed Flow, L/min	1.36(4)	1.34-1.39	1.28(4)	1.24-1.33	0.048(4)	0.045-0.056
PAC Flow, L/min	0	0-0	0	0-0	0	0-0
RS Flow, L/min	2.57(4)	2.27-2.8	2.52(4)	2.27-2.84	0.219(4)	0.189-0.248
RS Flow, % of Feed	189	167-206	197	179-214	456	420-517
Waste ML Flow, L/min	0.377(4)	0.304-0.463	0.375(4)	0.365-0.386	0.013(4)	0.012-0.013
HRT, days	3.03(4)	2.98-3.07	3.00(4)	2.91-3.10	2.77(4)	2.33-2.92
SRT, days	10.8(4)	8.6-13.0	9.5 (4)	9.2-9.8	8.5 (4)	6.9-10.3
Mixed Liquor Data						
Temp. , °C	31(12)	28.5-33	31.5(12)	29.5-33.5	21(12)	17-24
pH	*	7.02-7.74	*	7.10-7.66	*	7.54-7.90
Dissolved Oxygen, mg/L	3.2(15)	0-5.9	2.3(15)	0-5.8	5.3(18)	1.2-8.8
Suspended Solids, mg/L	4530(4)	4440-4760	4210(4)	3760-4480	4120(4)	4020-4240
SVI, ml/gm	221(1)		221(1)		221(1)	
Effluent Data						
TCOD, mg/L	901(4)	872-926	1030(4)	990-1070	1320(4)	1100-1640
SCOD, mg/L	771(4)	715-833	786(4)	721-851	862(4)	776-913
TOC, mg/L	255(1)		309(1)		340(1)	
NIBOD, mg/L	20(1)		25(1)		44(1)	
NISBOD, mg/L	**		9(1)		9(1)	
TSS, mg/L	66(4)	56-88	141(4)	124-162	341(4)	99-580
VSS, mg/L	55(4)	48-74	117(4)	100-138	265(4)	96-440

* Average pH not calculated.

** Analysis not performed.

solids and TCOD values in BTS-3 when the clarifier became full of solids. Slightly higher SCOD concentrations in the BTS-3 effluent are the result of the lower mixed liquor temperature.

PHASE 2 - PAC ADDITION AND ACCLIMATION

The addition of 200 mg/L PAC to BTS-1 and 800 mg/L PAC to BTS-2 influent was started on September 17, 1984. Additional single doses of PAC were added each day for ten days to bring the PAC concentrations in the aeration basin up to the expected equilibrium level. The concentrations of the single dosages were listed earlier in Table 4. At the same time, efforts were made to improve the performance of the BTS-3 clarifier and to maintain the temperature of BTS-3 near the temperatures of BTS-1 and BTS-2. Operation of all three units was continued at the same target operating parameters for 13 days after the last of the single doses of carbon was added to BTS-1 and BTS-2 on September 26, 1984.

Results from the operation of the three pilot units are shown graphically on Figures 25 to 32. Figure 25 shows the raw wastewater and effluent TCOD values during this phase. Figure 26 shows the effluent SCOD values. The high effluent TCOD values on Days 12, 13 and 27 for the BTS-3 effluent were the result of high effluent suspended solids (Figure 27) associated with efforts at adjusting clarifier flows and temperatures. The effect of the adjustments to the clarifier flows on Day 30 is seen by the increase in BTS-3 mixed liquor suspended solids after a period of general decline (Figure 28). The increase in the effluent TCOD values for Days 18,

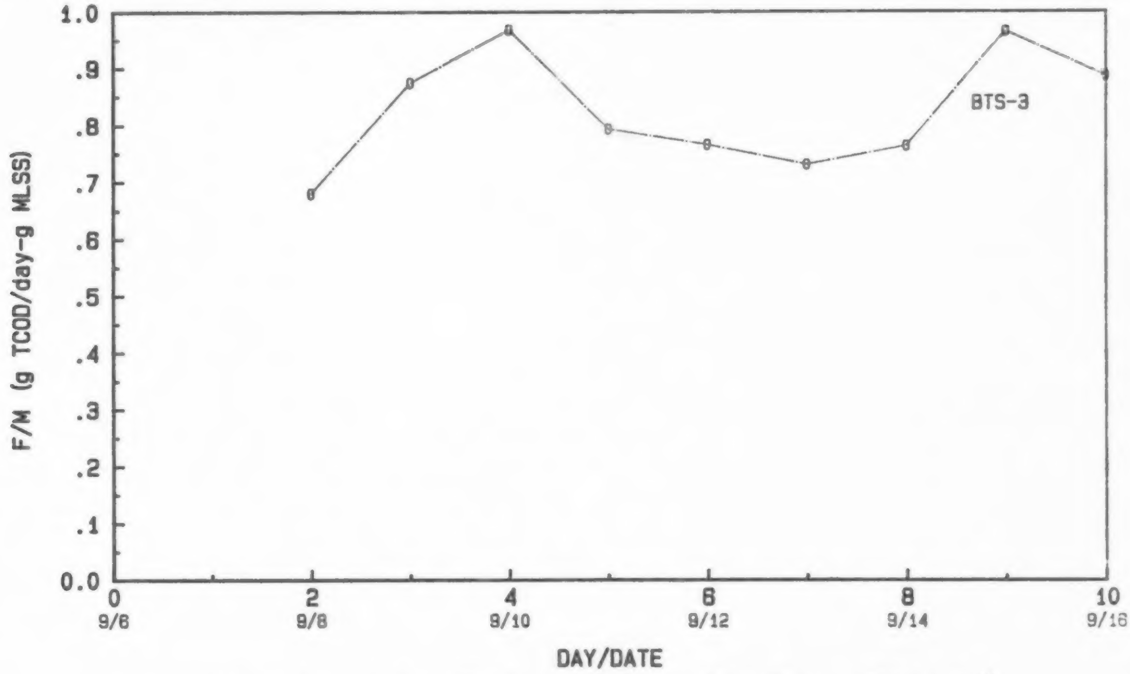


Figure 24. Pilot Plant Organic Loading Rates (Day 1-10).

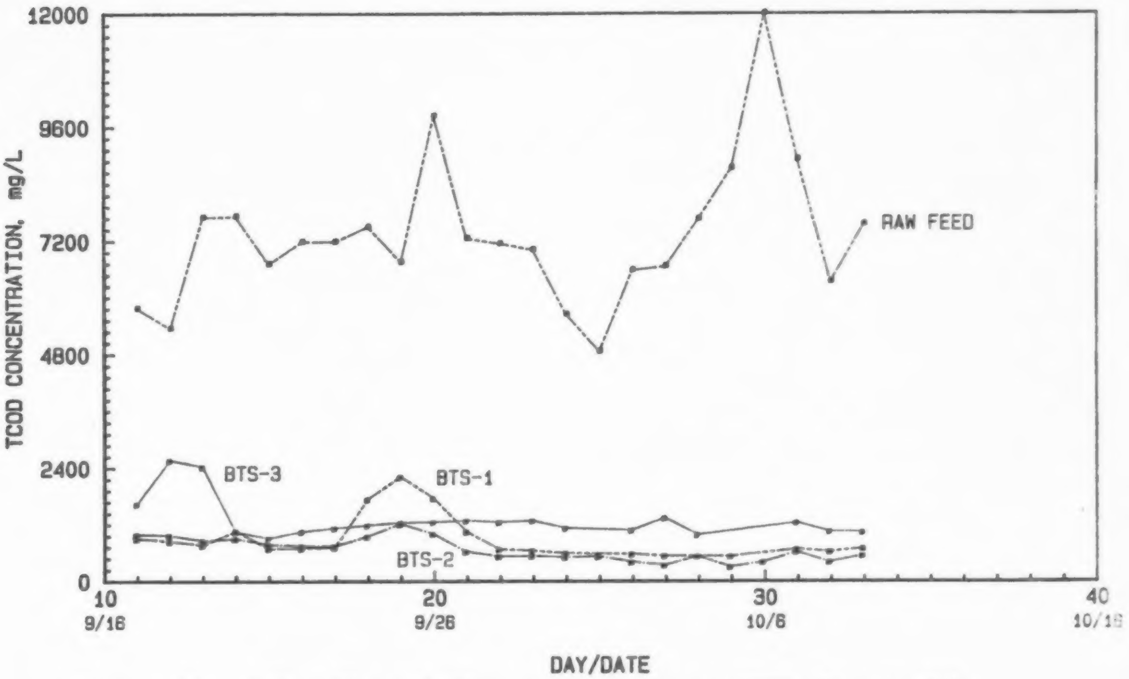


Figure 25. Pilot Plant Influent and Effluent TCOD (Day 11-33).

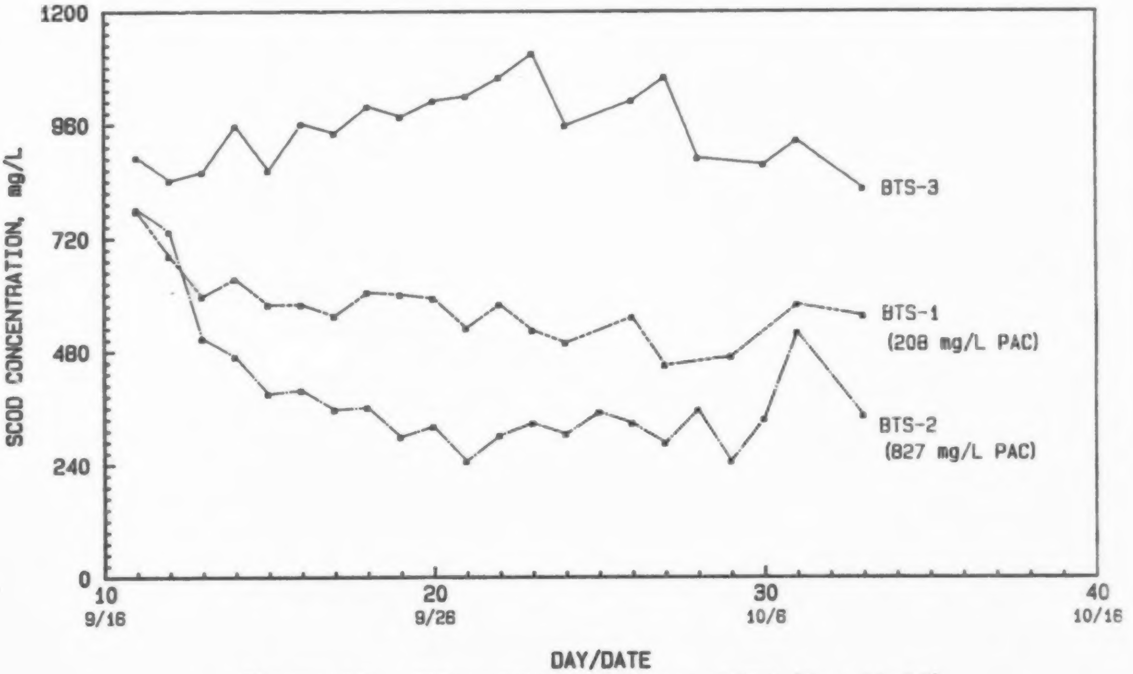


Figure 26. Pilot Plant Effluent SCOD (Day 11-33).

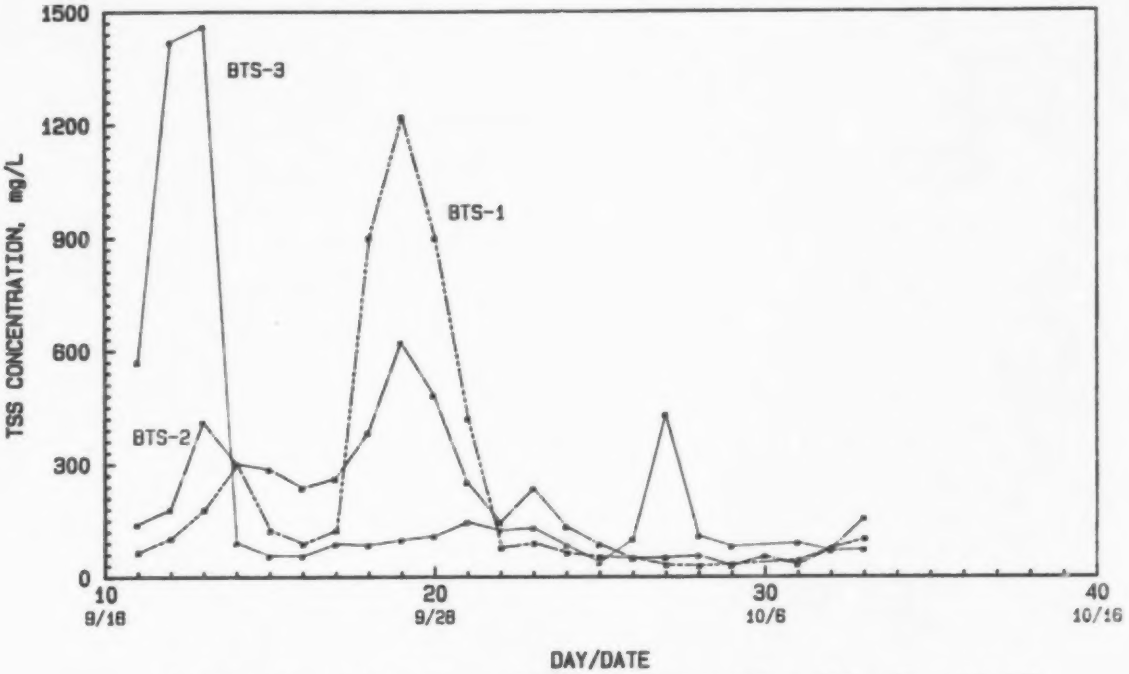


Figure 27. Pilot Plant Effluent Suspended Solids (Day 11-33).

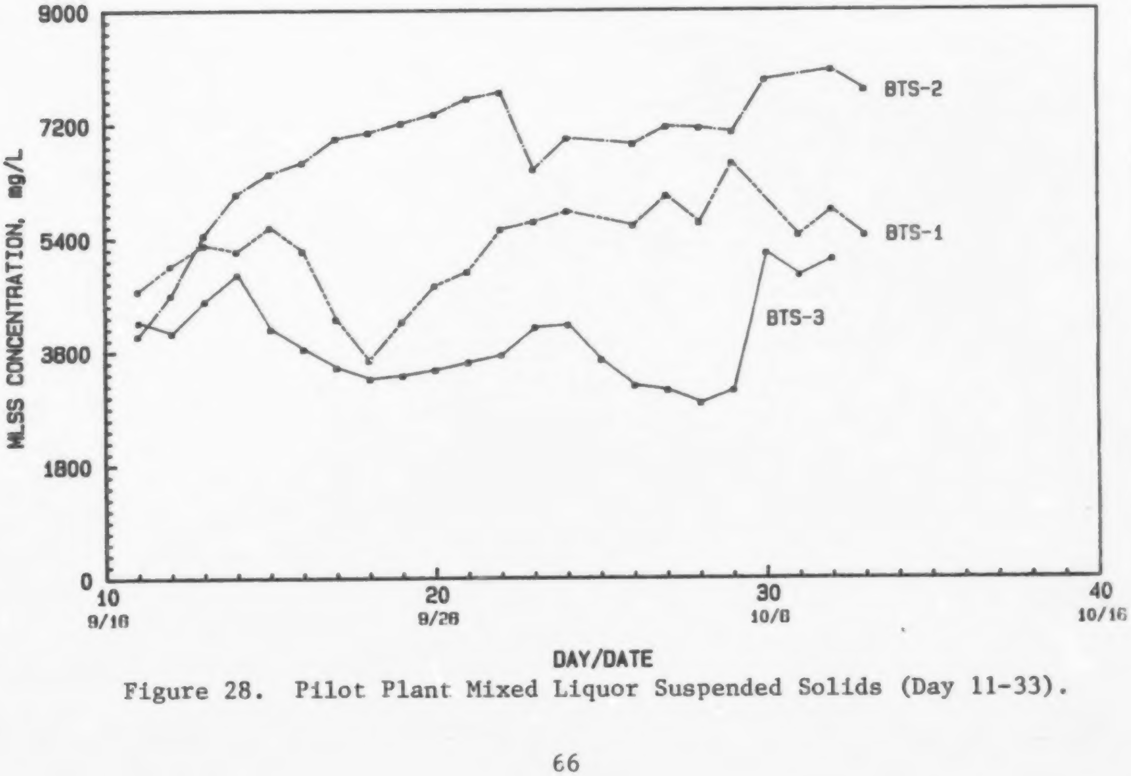


Figure 28. Pilot Plant Mixed Liquor Suspended Solids (Day 11-33).

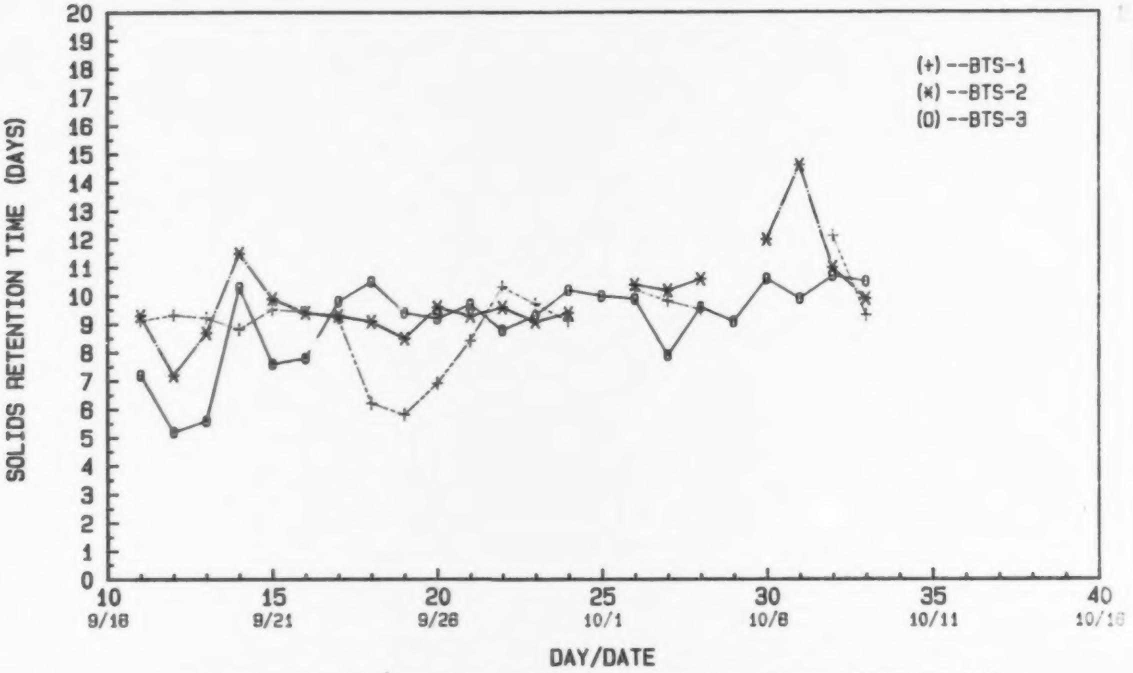


Figure 29. Pilot Plant Solids Retention Times (Day 11-33).

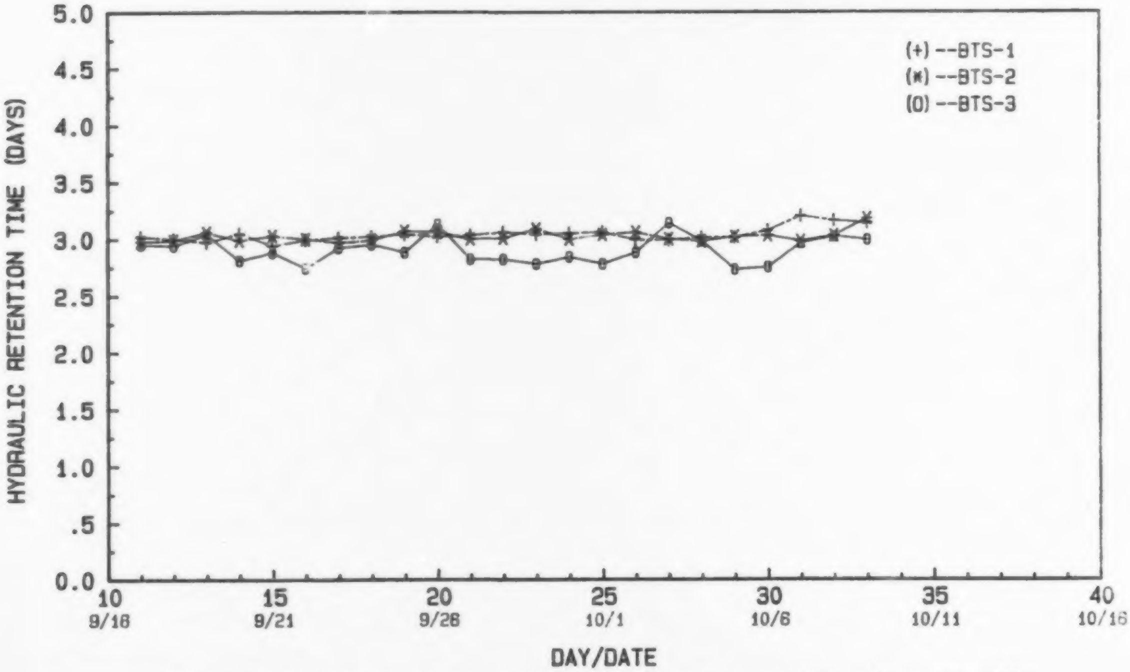


Figure 30. Pilot Plant Hydraulic Retention Times (Day 11-33).

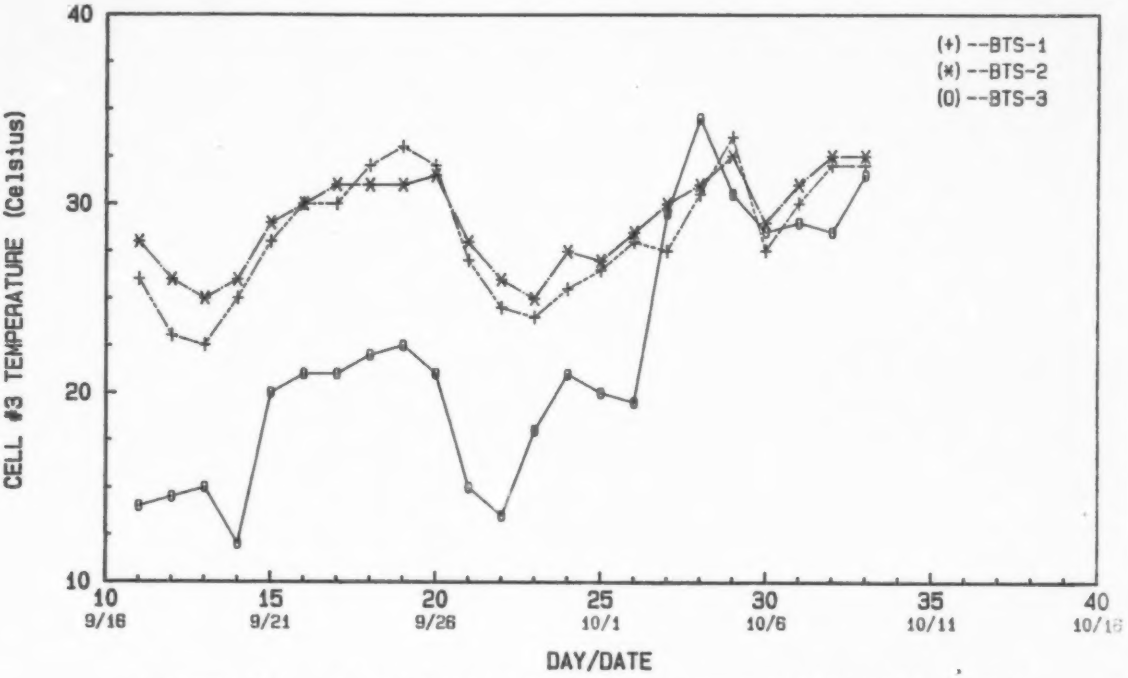


Figure 31. Pilot Plant Aeration Tank Temperature (Day 11-33).

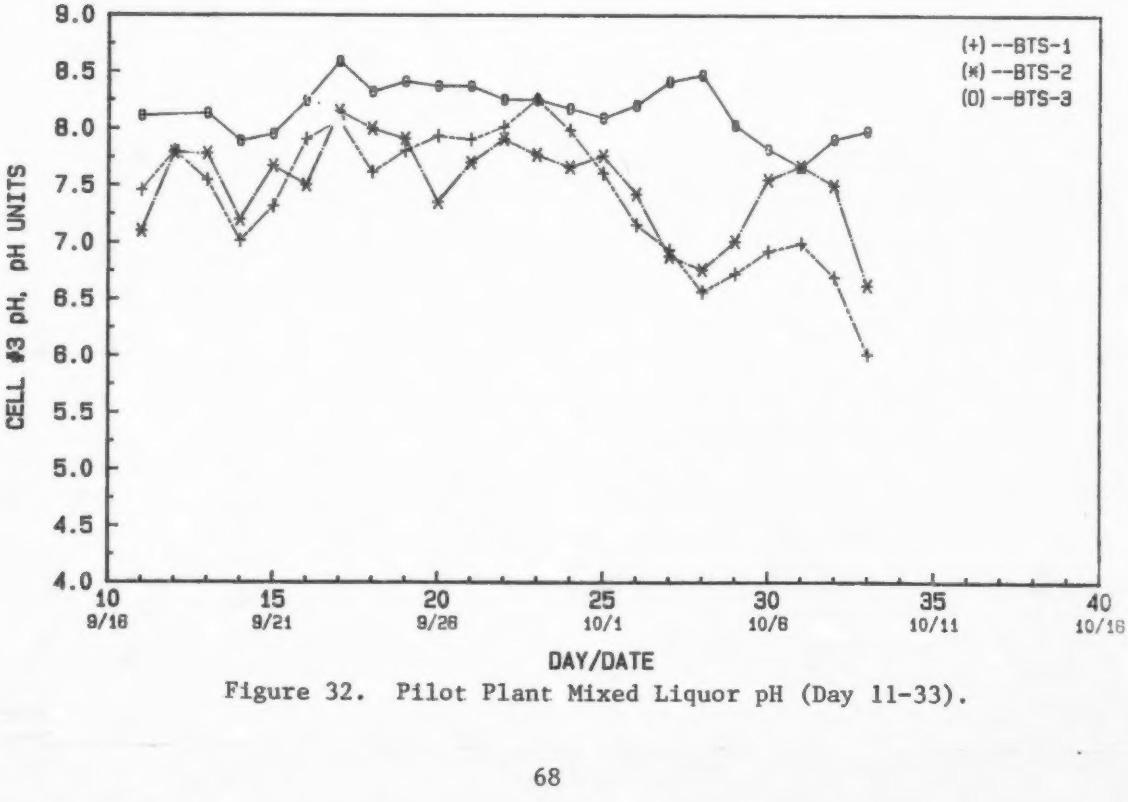


Figure 32. Pilot Plant Mixed Liquor pH (Day 11-33).

19 and 20 for BTS-1 (Figure 25) and the decrease in mixed liquor suspended solids for Days 16, 17, and 18 were attributed to a malfunctioning return sludge pump which allowed solids to accumulate in the BTS-1 clarifier. The motorized flushing valve on BTS-1 became stuck in the closed position during Day 29 causing the aeration tank to overflow. No mixed liquor was wasted on Day 30 to compensate for the solids lost in the overflow. A minor overflow of BTS-2 aeration tank caused by a plugged line to the clarifier also occurred on Day 29. Solids retention times based on daily volumes of mixed liquor wasted to the holding tanks plus effluent TSS are shown on Figure 29. Data are not included for days when additional solids were lost because of aeration tank overflows. Figure 30 shows the hydraulic retention time based on measured feed flows for each unit during this phase.

A summary of the operational parameters and analytical data for the last 13 days of this phase is presented in Table 20. These data show that the PAC dosages, hydraulic retention time and solids retention time were reasonably close to the planned values. Mixed liquor temperatures were similar for BTS-1 and BTS-2 and the low temperature of BTS-3 was corrected (Figure 31). The pH of the BTS-1 and BTS-2 mixed liquor generally decreased during the latter 13 days of this phase (Figure 32) probably as a result of nitrification. It was more difficult to keep the desired dissolved oxygen level in BTS-2 than the other units. Only one of the 60 dissolved oxygen measurements in BTS-1 and 8 of 63 measured values in BTS-3 were less than 1.5 mg/L. For BTS-2, however, 26 of 60 dissolved oxygen measurements were less than 1.5 mg/L and 17 were less than 1 mg/L.

The summary of the effluent analytical data in Table 20 shows that added PAC was effective in reducing TCOD, TOC and NIBOD concentrations. The degree of effectiveness of PAC on effluent quality and process operation was studied in Phase 3.

PHASE 3 - INTENSIVE TEST PERIOD

Operation of the three pilot plants continued at the same target operating levels during the Phase 3 Intensive Test period. The frequency of flow and in-situ data measurements was increased during this period. Oxygen uptake rates were also performed on each aeration tank cell each day.

Pilot Plant Operation

A summary of pilot plant operation data for this period is presented in Table 21. Feed flows were controlled so that hydraulic retention times (HRT) for all units were reasonably close to the desired 3 day level (Figure 33). The solids retention times were also relatively close to the 10 day goal. Figure 34 shows the SRT values based on the daily volume of mixed liquor wasted and effluent suspended solids. The BTS-1 waste mixed liquor pump failed on Day 39 resulting in a very low volume of wasted mix liquor and a very high calculated SRT for that date. The pump was replaced on Day 40 and mixed liquor was wasted at a rate such that the average SRT for Days 39 and 40 was 10 days. The calculated daily SRT values for BTS-1 on Days 39 and 40 are not shown on Figure 34. Temperatures were relatively consistent

TABLE 20. SUMMARY OF BIOLOGICAL PILOT PLANT OPERATION AT END OF ACCLIMATION PERIOD (DAY 21-33, SEPTEMBER 27-OCTOBER 9, 1984)

Parameter	BTS-1		BTS-2		BTS-3	
	Average (n)	Range	Average (n)	Range	Average (n)	Range
Operational Data						
Feed Flow, L/min	1.35(13)	1.29-1.38	1.26(13)	1.18-1.32	0.044(14)	0.036-0.049
PAC Flow, ml/min	17.5(13)	9.9-18.8	18.4(13)	18.0-18.6	*	
RS Flow, L/min	4.03(13)	3.79-4.54	3.30(13)	1.72-4.90	0.209(13)	0.190-0.226
RS Flow, % of Feed	298	281-352	262	132-383	475	404-525
Waste ML Flow, ml/min	330(13)	0**-443	348(13)	221-392	13(13)	12-14
PAC Dosage, mg/L	197(13)	112-218	775(13)	243-861	0	0
F/M, g TCOD/day-g MLSS	***		***		0.75(5)	0.56-0.89
F/M, g TBOD/day-g MLSS	***		***		0.31(2)	0.29-0.34
HRT, days	3.06(13)	2.99-3.16	3.03(13)	2.98-3.18	2.88(13)	2.73-3.14
SRT, days	9.8(9)	8.4-12.1	10.6(11)	9.1-14.6	9.7(13)	7.9-10.7
Mixed Liquor Data						
Temp., °C	28.5(39)	24-34	29.5(39)	26-33	24.5(39)	13.5-34.5
pH	#	6.0-8.2	#	6.6-7.9	#	7.4-8.5
DO, mg/L	4.5(60)	0.9-7.5	2.4(60)	0.0-5.6	3.3(63)	0.6-5.4
TSS, mg/L	5720(12)	4860-6580	7400(12)	6480-8160	3870(13)	2780-5160
SVI, ml/gm	174(7)	144-214	140(6)	124-184	268(8)	194-332

(continued)

TABLE 20. (continued)

Parameter	BTS-1 Average (n)	BTS-1 Range	BTS-2 Average (n)	BTS-2 Range	BTS-3 Average (n)	BTS-3 Range
Effluent Data						
TCOD, mg/L	660(12)	530-1060	497(13)	316-632	1190(10)	1000-1360
SCOD, mg/L	530(11)	449-659	329(12)	247-520	973(10)	824-1060
TOC, mg/L	196(6)	138-390	109(5)	76-137	320(6)	287-360
NIBOD, mg/L	12(2)	9-15	6(2)	5-7	54(2)	42-67
NISBOD, mg/L	6(2)	4-8	4(2)	4-5	22(2)	16-27
TSS, mg/L	86(13)	27-420	103(13)	28-250	155(13)	38-545
VSS, mg/L	85(6)	27-240	100(6)	23-198	120(6)	35-330

* No PAC added to BTS-3

** Mixed liquor deliberately not wasted on Day 30 to compensate for solids lost during aeration tank overflow.

*** F/M ratios not calculated for BTS-1 and BTS-2 because of PAC in mixed liquor.

# Average pH values not calculated.

TABLE 21. SUMMARY OF BIOLOGICAL PILOT PLANT OPERATION INTENSIVE TEST PERIOD (DAY 34-47, OCTOBER 10-23,1984)

Parameter	BTS-1		BTS-2		BTS-3	
	Average (n)	Range	Average (n)	Range	Average (n)	Range
Operational Data						
Feed Flow, L/min	1.34(14)	1.25-1.38	1.26(14)	1.18-1.32	0.044(14)	0.036-0.049
PAC Flow, ml/min	18(14)	18-19	18(14)	18-19	*	
RS Flow, L/min	3.01(14)	1.95-5.18	4.08(14)	2.27-6.49	0.163(14)	0.089-0.211
RS Flow, % of Feed	225	148-411	324	177-511	370	202-567
Waste ML Flow, ml/min	420(14)	68-758	367(14)	340-389	13(14)	11-15
PAC Dosage, mg/L	208(14)	198-222	827(14)	798-884	0	-
F/M, g TCOD/day-g MLSS	**	**	**	**	0.64(13)	0.49-0.91
F/M, g TBOD/day-g MLSS	**	**	**	**	0.20(4)	0.14-0.28
HRT, days	3.08(14)	2.99-3.29	3.06(14)	2.93-3.22	3.01(14)	2.66-3.64
SRT, days	9.5(12)	9.0-9.9	10.0(13)	8.9-10.7	9.4 (13)	8.0-10.7
Mixed Liquor Data						
Temp., ^{o}C	32.5(84)	30.5-35	32(84)	30-34	31.5(84)	25.5-33.5
pH	***	4.1-7.5	***	4.5-7.7	***	6.0-8.7
DO, mg/L	3.3(84)	0.7-6.2	3.4(84)	0.3-6.6	4.3(84)	0.4-6.4
TSS, mg/L	5850(14)	5350-7000	7690(13)	6620-8300	4790(13)	4040-6340
SVI, ml/g	171(13)	147-180	130(13)	118-157	204(13)	158-245

(continued)

TABLE 21. (continued)

Parameter	BTS-1		BTS-2		BTS-3	
	Average (n)	Range	Average (n)	Range	Average (n)	Range
O_2 Uptake Rate, mg/L-min	0.83(42)	0.38-1.58	0.83(42)	0.48-1.9	0.95(42)	0.5-1.48
Settling Rate, cm/min	0.032 (13)	0.006-0.098	0.045(11)	0.003-0.128	0.007 (13)	0.000-0.021
Effluent Data						
TCOD, mg/L	585(14)	504-679	532(14)	356-750	1070(14)	894-1190
SCOD, mg/L	459(14)	419-497	265(14)	216-347	825(14)	684-929
TOC, mg/L	158(14)	133-195	110(14)	96-151	290(14)	265-363
NIBOD, mg/L	16(6)	8-33	15(6)	8-21	27(6)	16-38
NISBOD, mg/L	<6	<3-17	<5(6)	<2-15	<8(6)	5-16
TSS, mg/L	85(14)	47-222	190(14)	64-330	143(14)	89-273
VSS, mg/L	60(14)	41-122	158(14)	54-278	109(14)	55-227

* PAC not added to BTS-3.

** F/M ratios not calculated for BTS-1 and BTS-2 because of PAC in mixed liquor.

*** Average pH values not calculated.

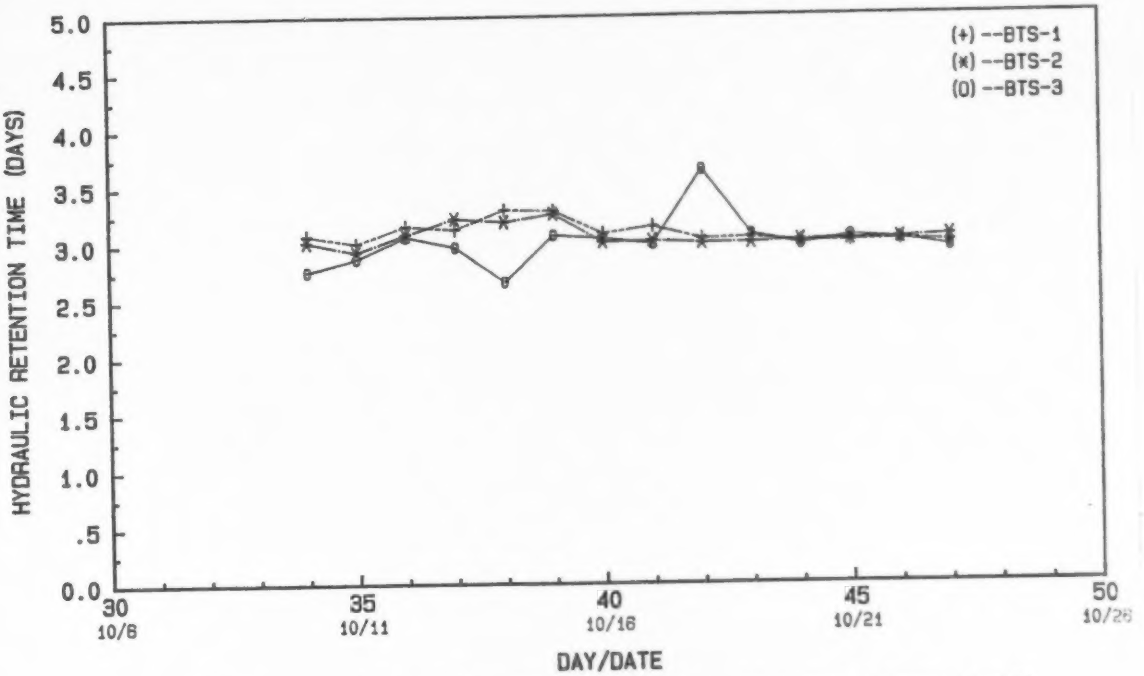


Figure 33. Pilot Plant Hydraulic Retention Time (Day 34-47).

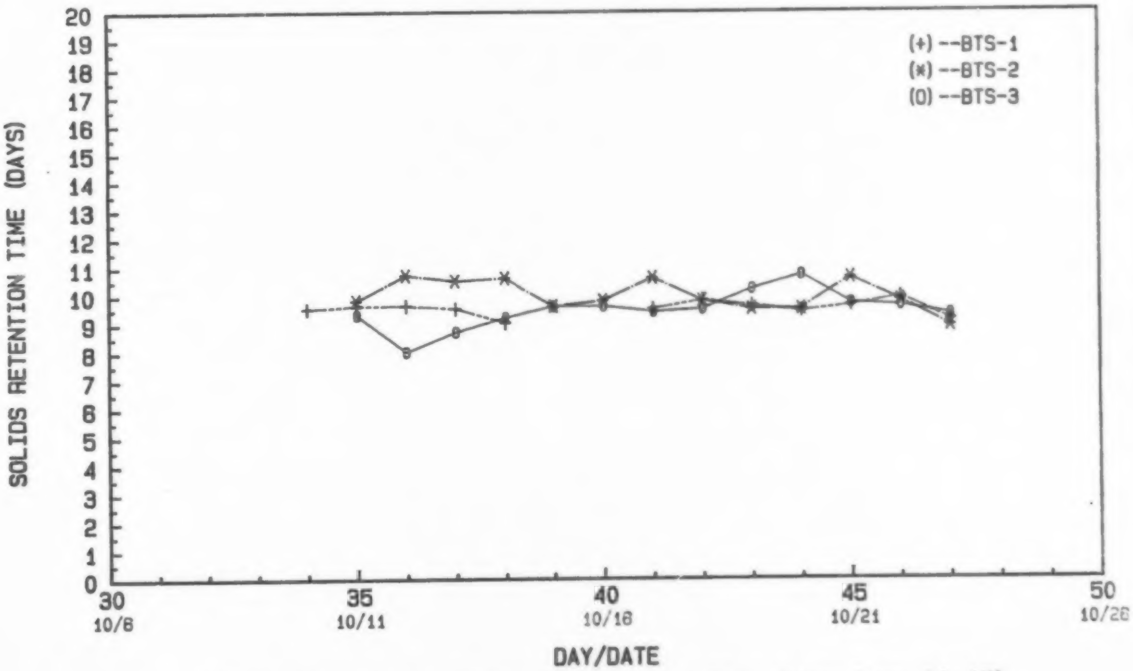


Figure 34. Pilot Plant Solids Retention Time (Day 34-47).

in all three units during this period (Figure 35). A suitable method of controlling BTS-3 temperature was still being sought at the start of this test phase. On Day 36, one heat tape and one thermostatically controlled aquarium heater were installed in each aeration cell of BTS-3. This system was used for the remainder of the pilot tests. The variation in mixed liquor suspended solids during this period is shown on Figure 36.

The dissolved oxygen concentrations in each cell of each unit are shown on Figures 37 to 39. The values plotted for each day are the average of the two dissolved oxygen measurements made in each cell each day. The dissolved oxygen content of the mixed liquor depended upon the oxygen uptake rate and the ability to supply enough air to satisfy the uptake rate. Both BTS-1 and BTS-2 were using nearly all the available air. Because the pressure drop across the air throttling valve to each cell was very low, it was very difficult to balance the dissolved oxygen concentrations in each cell. During this phase, cell 3 of BTS-1 and cell 2 of BTS-2 usually had the lowest dissolved oxygen concentration for their respective pilot units. High pressure air used for BTS-3 allowed for better distribution to maintain the mixed liquor dissolved oxygen at 2 mg/L or greater. The reduced oxygen levels on Days 39 and 40 in all 3 pilot plants were associated with abnormally high TCOD in the raw wastewater on those days (Figure 40).

The oxygen uptake rates for each cell of each pilot unit are shown on Figures 41 to 43. As expected, the uptake rates for cell 1 of each pilot

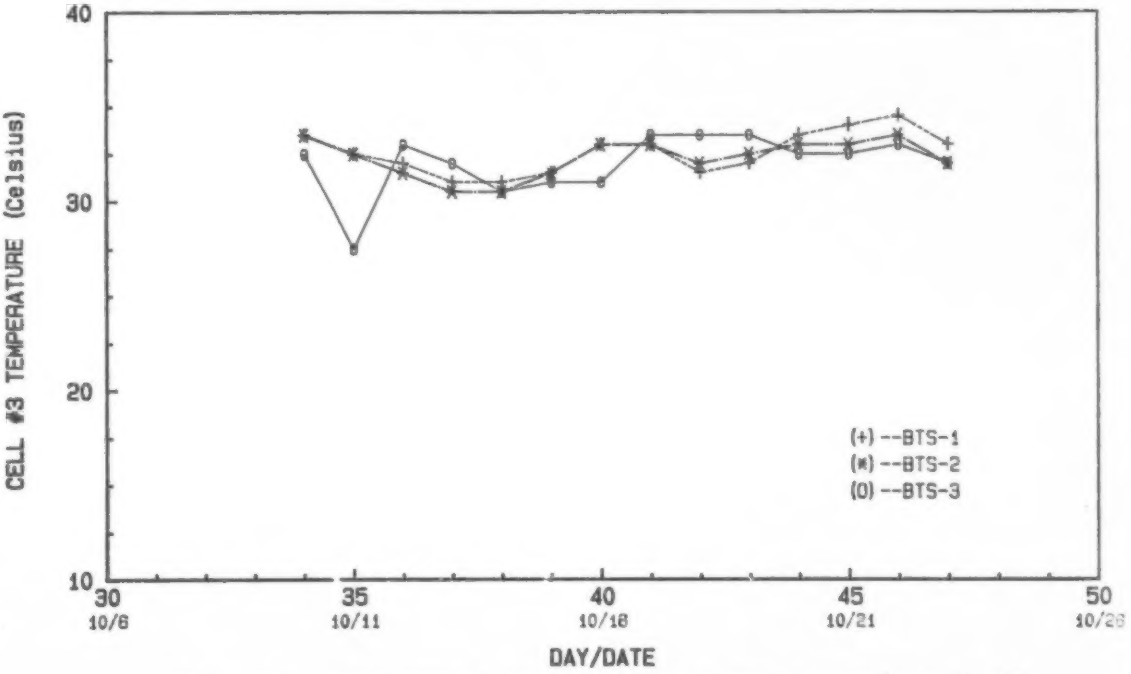


Figure 35. Pilot Plant Aeration Tank Temperature (Day 34-47).

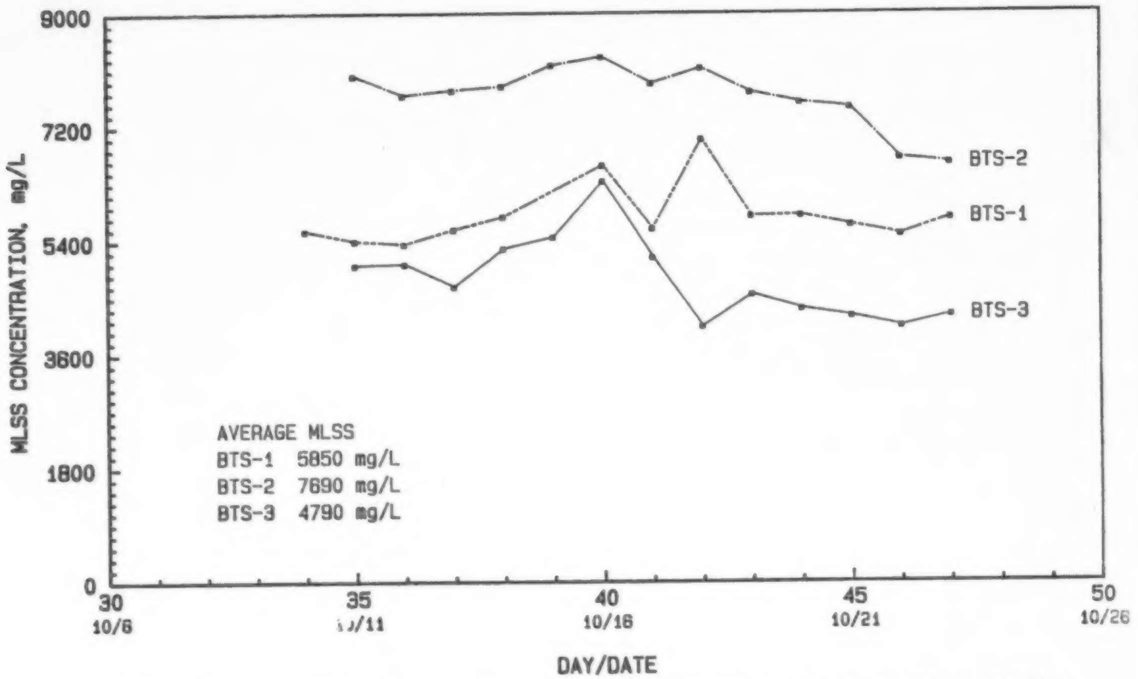


Figure 36. Pilot Plant Mixed Liquor Suspended Solids (Day 34-47).

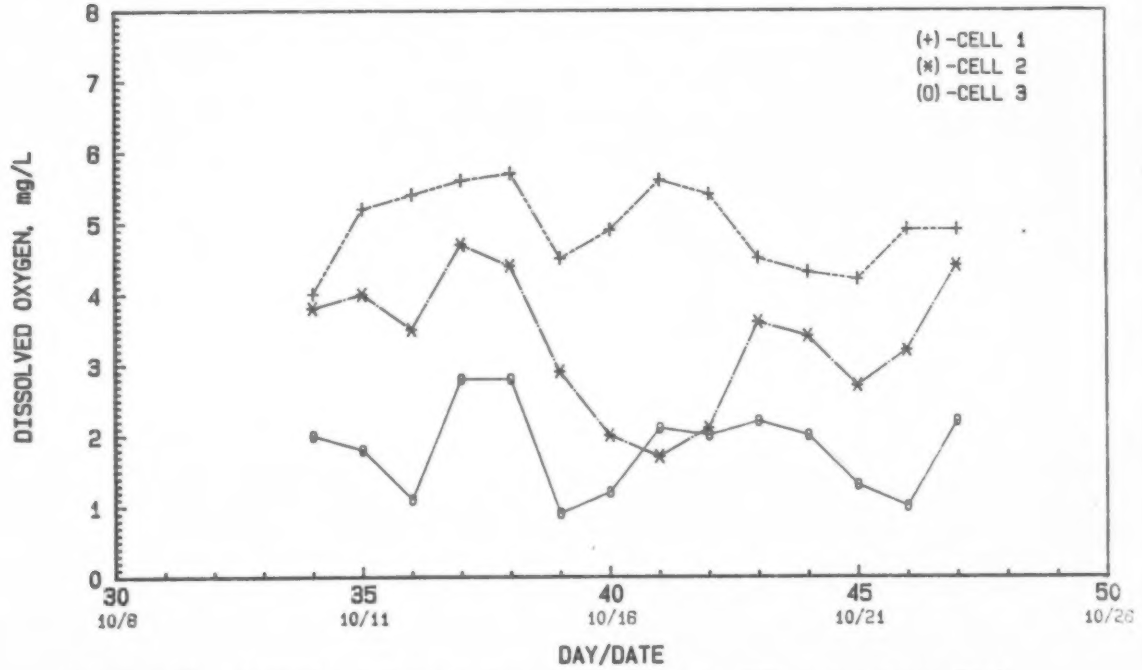


Figure 37. Dissolved Oxygen Concentrations in BTS-1 Aeration Tank (Day 34-47).

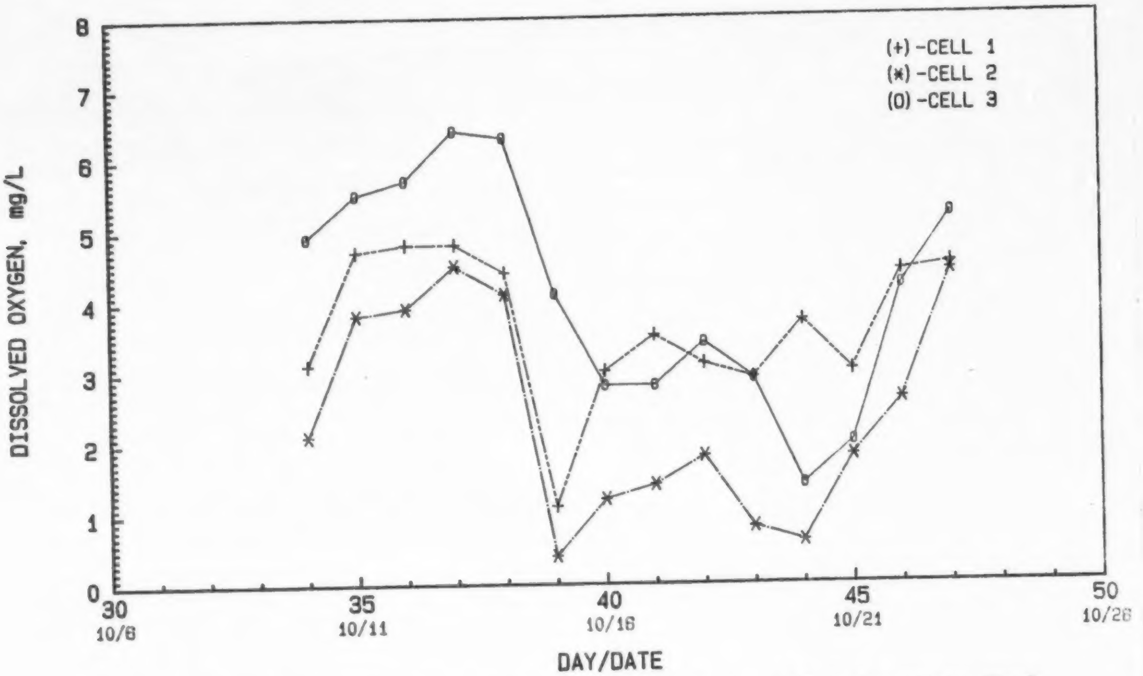


Figure 38. Dissolved Oxygen Concentrations in BTS-2 Aeration Tank (Day 34-47).

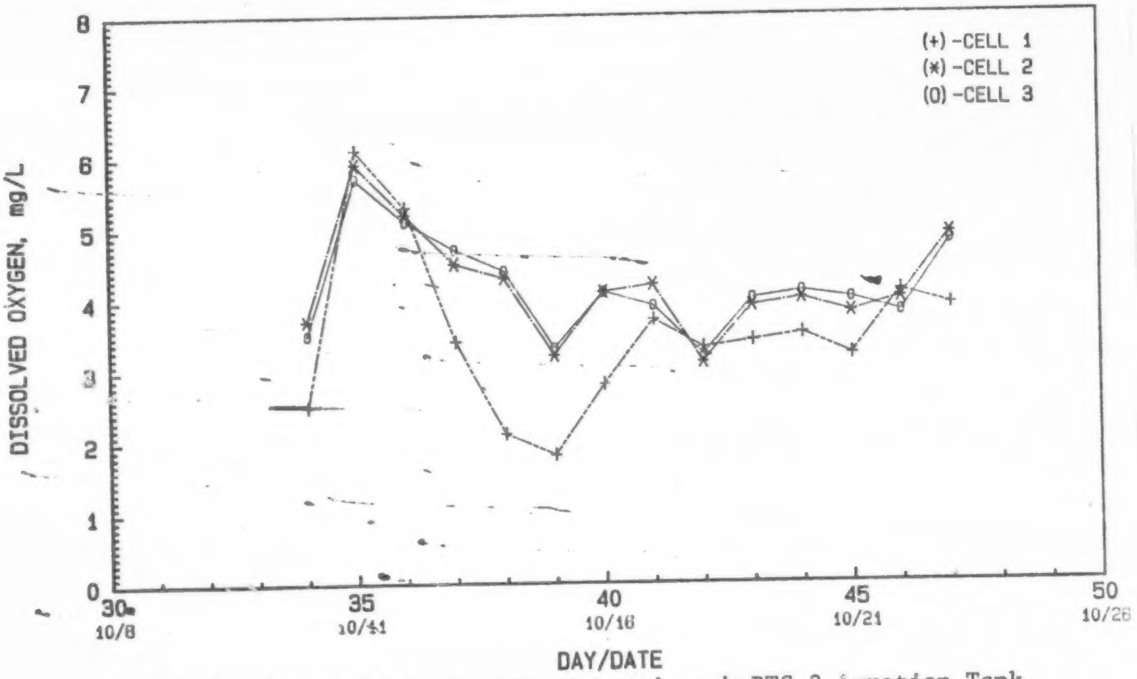


Figure 39. Dissolved Oxygen Concentrations in BTS-3 Aeration Tank (Day 34-47).

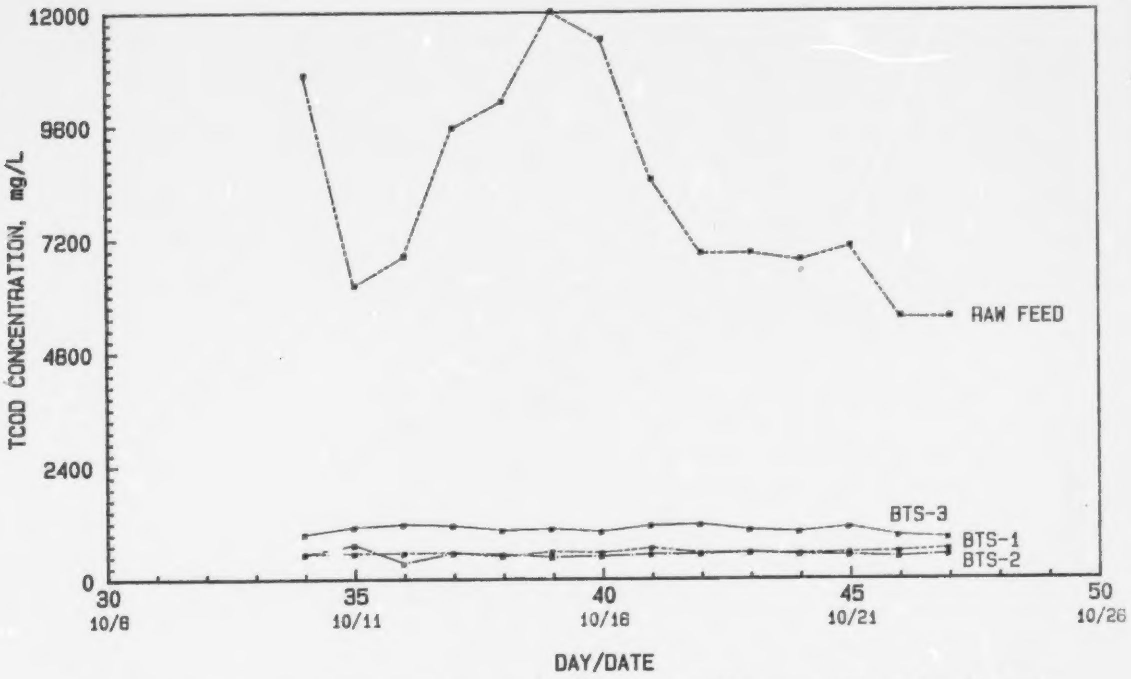


Figure 40. Pilot Plant Influent and Effluent TCOD (Day 34-47).

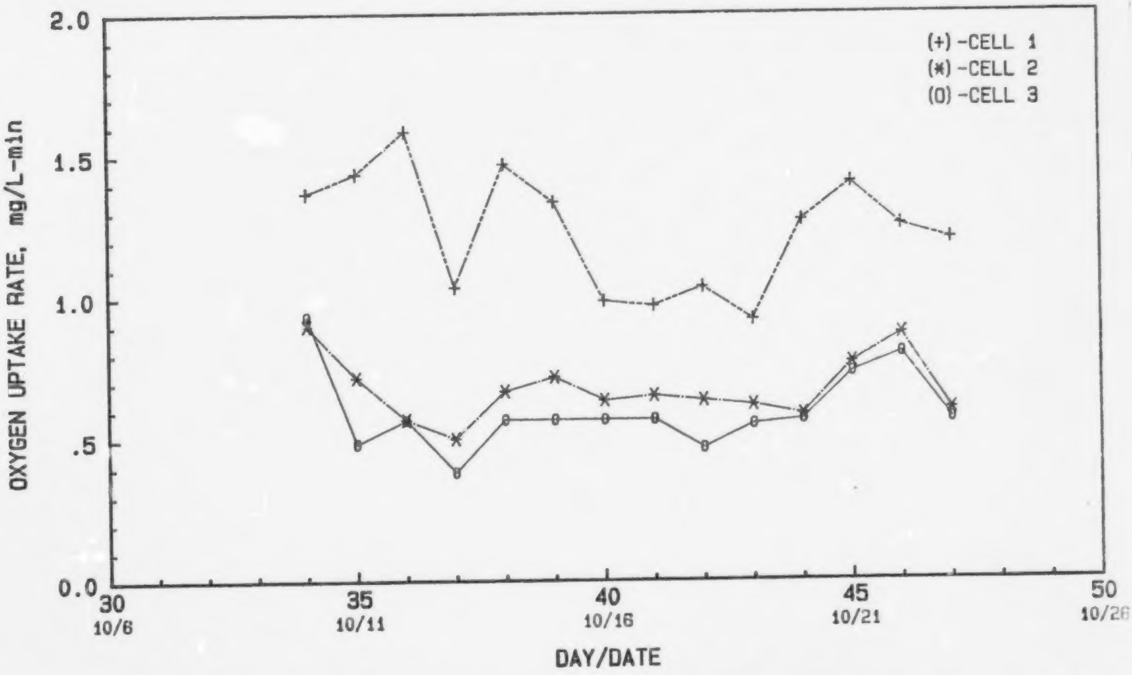


Figure 41. Oxygen Uptake Rate - BTS-1 (Day 34-47).

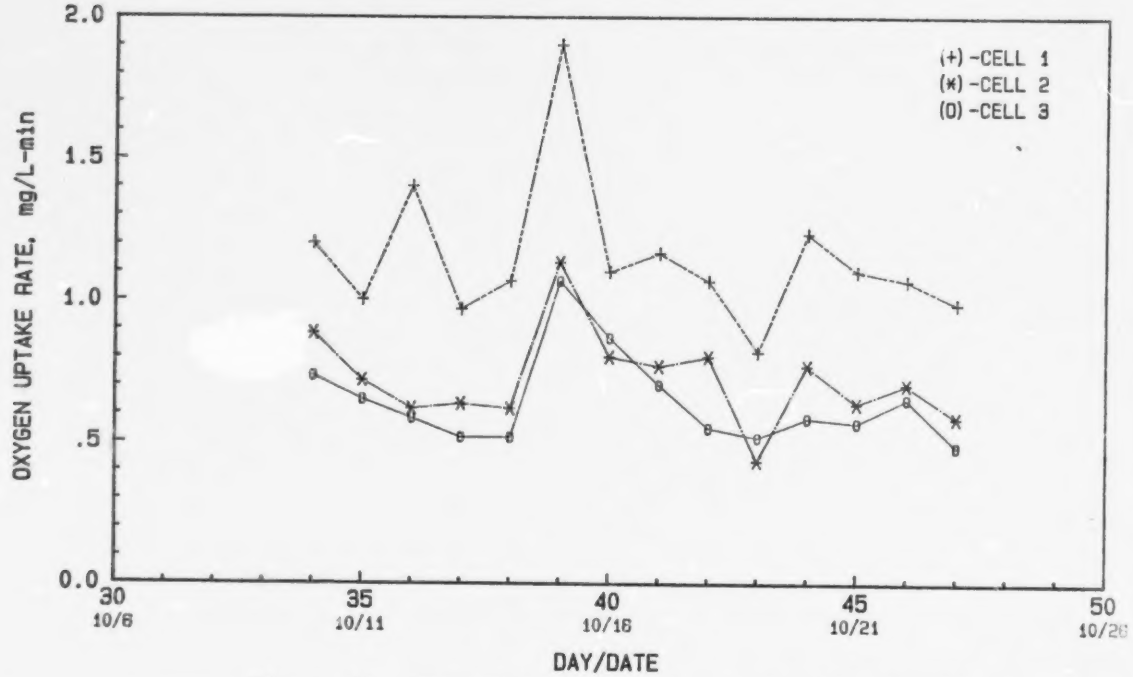


Figure 42. Oxygen Uptake Rate - BTS-2 (Day 34-47).

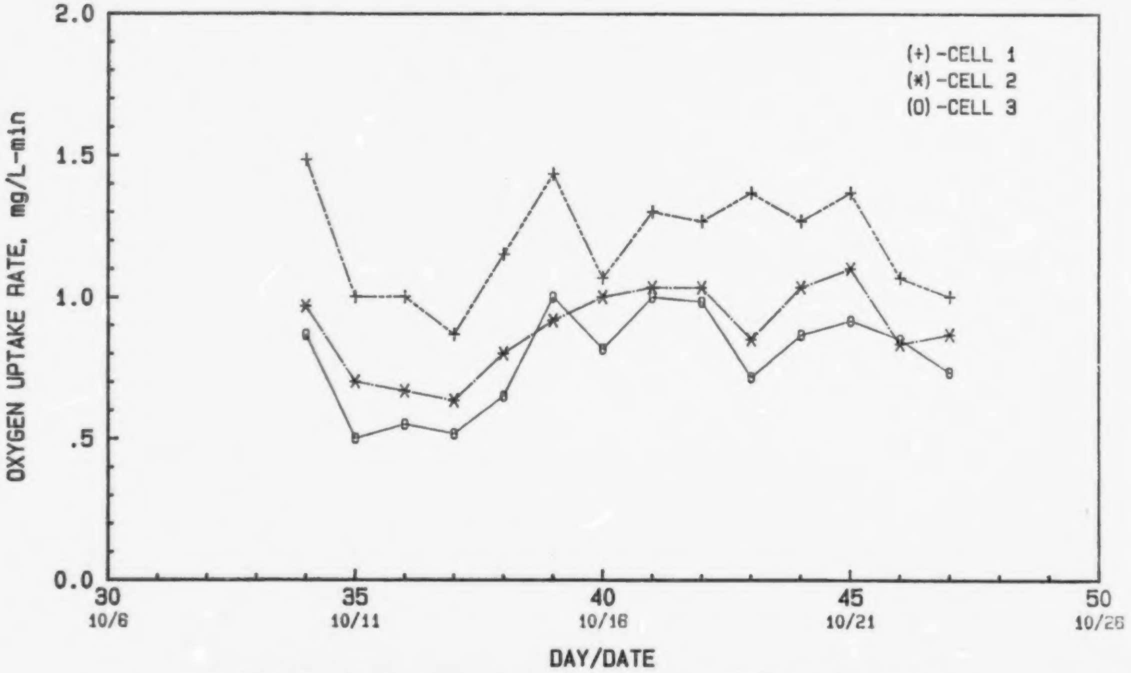


Figure 43. Oxygen Uptake Rate - BTS-3 (Day 34-47).

unit were greater than for cells 2 and 3, although the difference between cell 1 and the other cells was not as great for BTS-3 as for the pilot units containing PAC. The high influent TCOD on Day 39 had a greater effect on oxygen uptake rate for BTS-2 (the unit with the 827 mg/L PAC dosage) than the other two pilot units. The average oxygen uptake rate, however, was similar for all three pilot units during the intensive test period (Table 21).

The pH values of BTS-1 and BTS-2 mixed liquor started to decrease about one week before the start of the intensive test phase (Figure 32). This decrease continued for the first four days of the intensive test phase, reaching a low value of pH 6.0 in BTS-2 and less than 6 in BTS-1 (Figures 44 and 45). The mixed liquor pH then increased for several days before starting to decrease again. The pH of BTS-3 mixed liquor which had remained in the 7.5 to 8.5 pH range, also started to decrease at the beginning of the intensive test period (Figure 46). By Day 42, the BTS-3 mixed liquor pH was similar to that of the other units (Figure 47). Addition of dilute sodium hydroxide was started on Day 44 with the objective of raising the mixed liquor pH to 7. The caustic was added manually as a dilute solution to bring the pH up gradually. On Day 46, however, a slug of low pH feed wastewater (pH = 1.2) entered the pilot units. The feed flow was stopped as soon as the low pH was discovered. The pH of the mixed liquor was reduced to 4.0 and 4.5 in cell 1 of BTS-1 and BTS-2, respectively. Both units produced a large amount of foam. Although the mixed liquor pH of BTS-3 was also depressed, feed flow was stopped before the low pH levels of BTS-1 and BTS-2 were reached. All available caustic was added to BTS-1 and BTS-2 and sludge was returned continuously for a short period to restore the pH of cell 1 to more acceptable levels. Feed flow was resumed when the feed pH returned to normal. Additional caustic was obtained and added to all three units to bring the pH in all cells to about pH 6.5. The continuous addition of sodium hydroxide to all units was started on Day 47 in an effort to maintain mixed liquor pH near 7.0.

The mixed liquor sludge volume index (SVI) was relatively uniform for BTS-1 and BTS-2 for the intensive test period (Figure 48). The SVI for the BTS-3 mixed liquor, however, increased during the latter part of this period. In spite of the increase in measured SVI for BTS-3, routine scraping of the clarifier sides improved performance to the point where one clarifier was taken out of service on Day 37 and only one clarifier was used for the remainder of the tests. The sludge blanket depth in the single clarifier used after Day 37 gradually decreased even as the measured SVI increased. It should be noted, however, that the pilot unit clarifiers were greatly oversized for the flows used in these tests. The average clarifier overflow rates for BTS-1, BTS-2 and BTS-3 were 1470, 1385 and 367 L/m^2-day, respectively based upon influent feed rates.

The MLSS settling rates were very low. The settling rate for BTS-1 was relatively high for the first several days of the intensive test period but was typically less than 0.03 cm/min from Day 38 through 47 (Figure 49). The average values for settling rate listed in Table 21 represent all measurements in the intensive test phase.

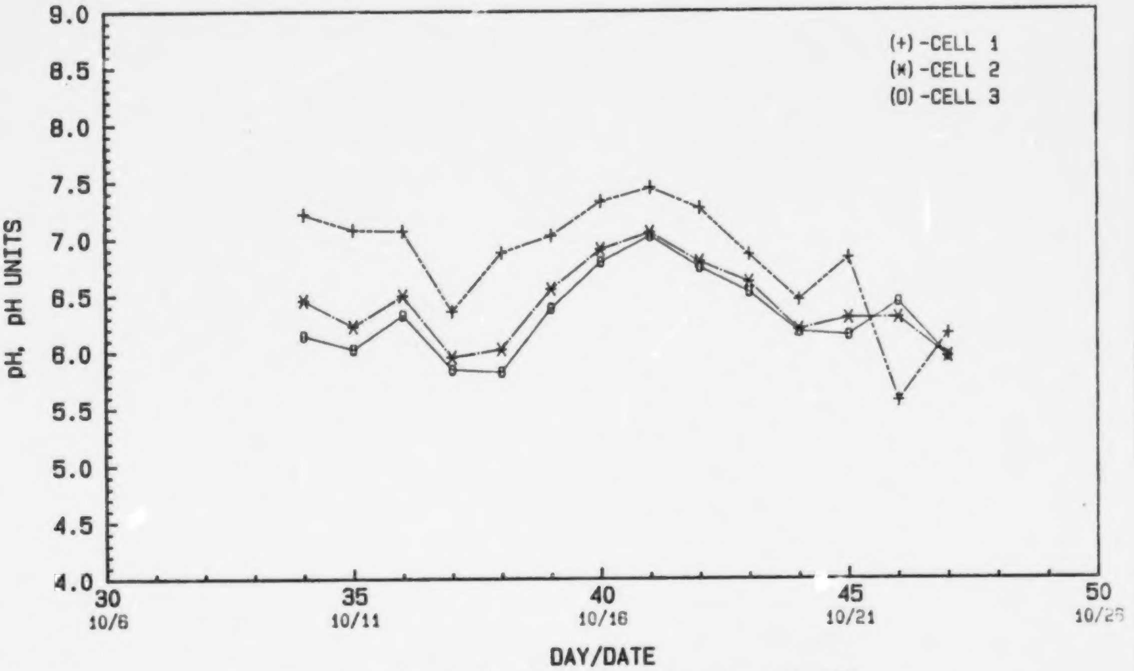


Figure 44. BTS-1 Mixed Liquor pH (Day 34-47).

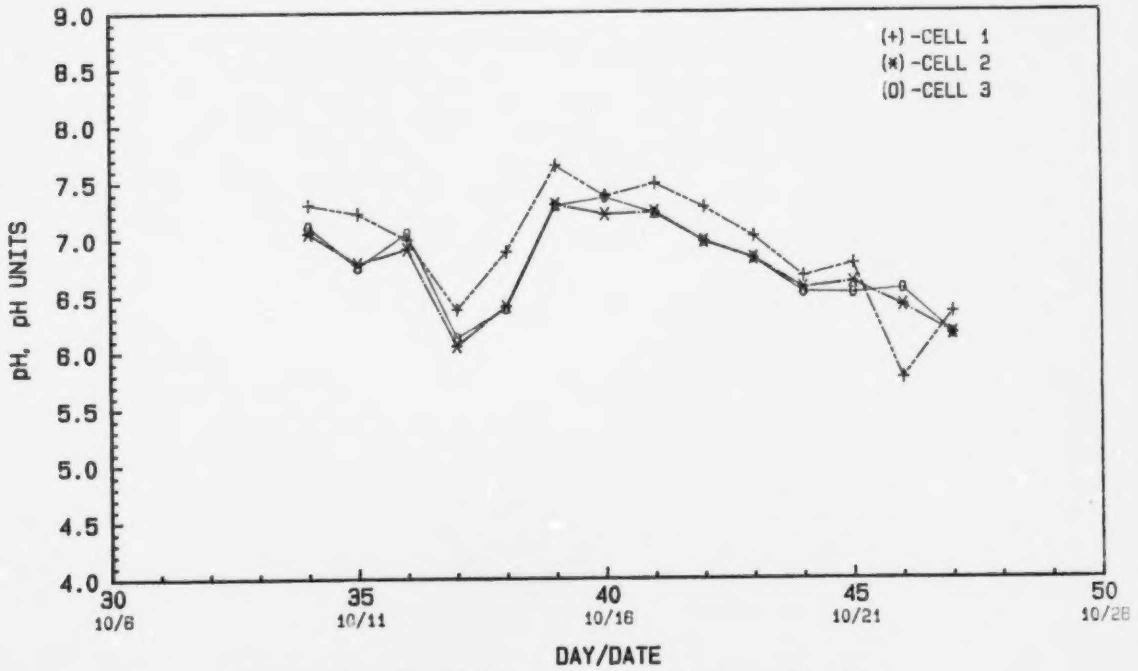


Figure 45. BTS-2 Mixed Liquor pH (Day 34-47).

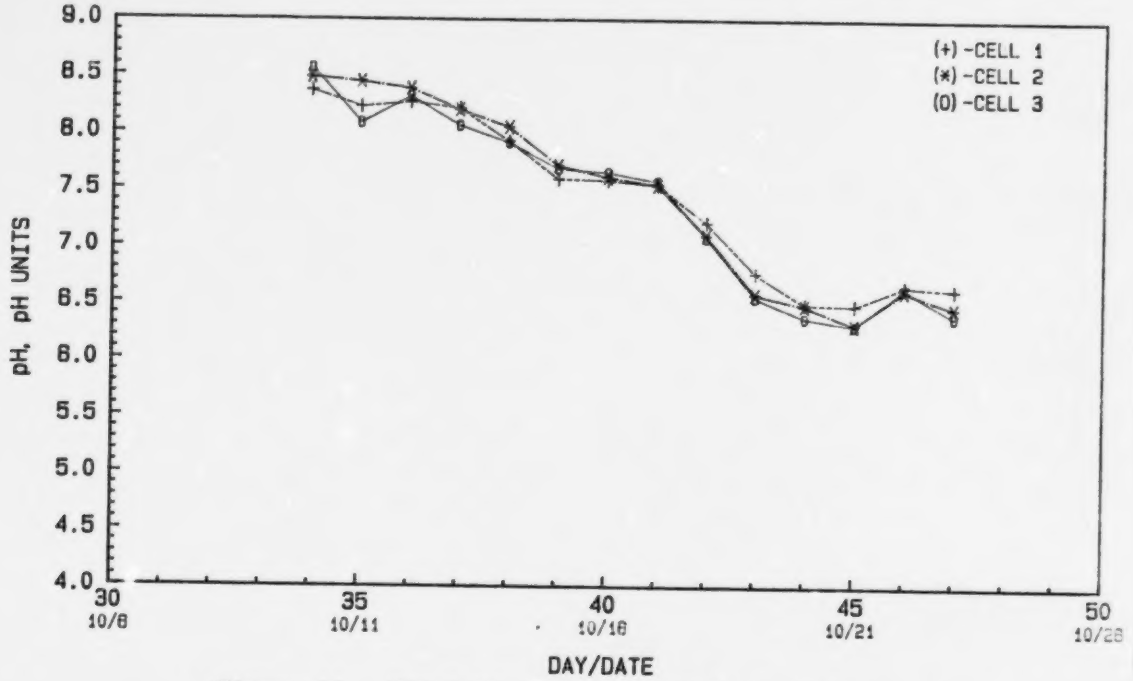


Figure 46. BTS-3 Mixed Liquor pH (Day 34-47).

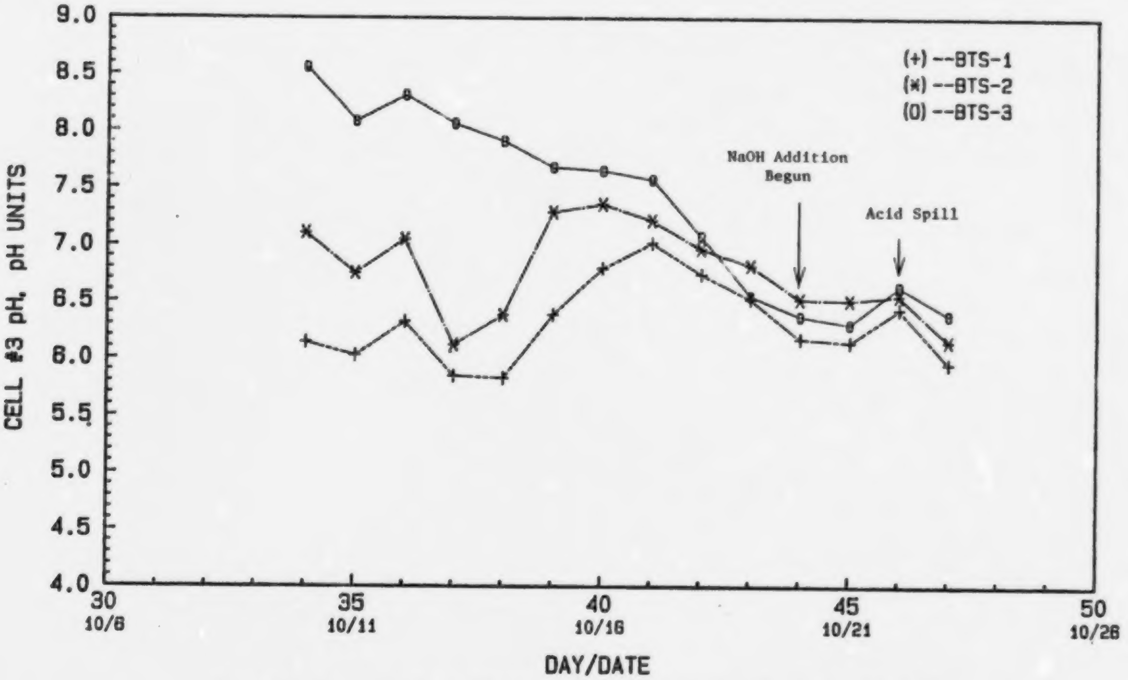


Figure 47. Pilot Plant Mixed Liquor pH (Day 34-47).

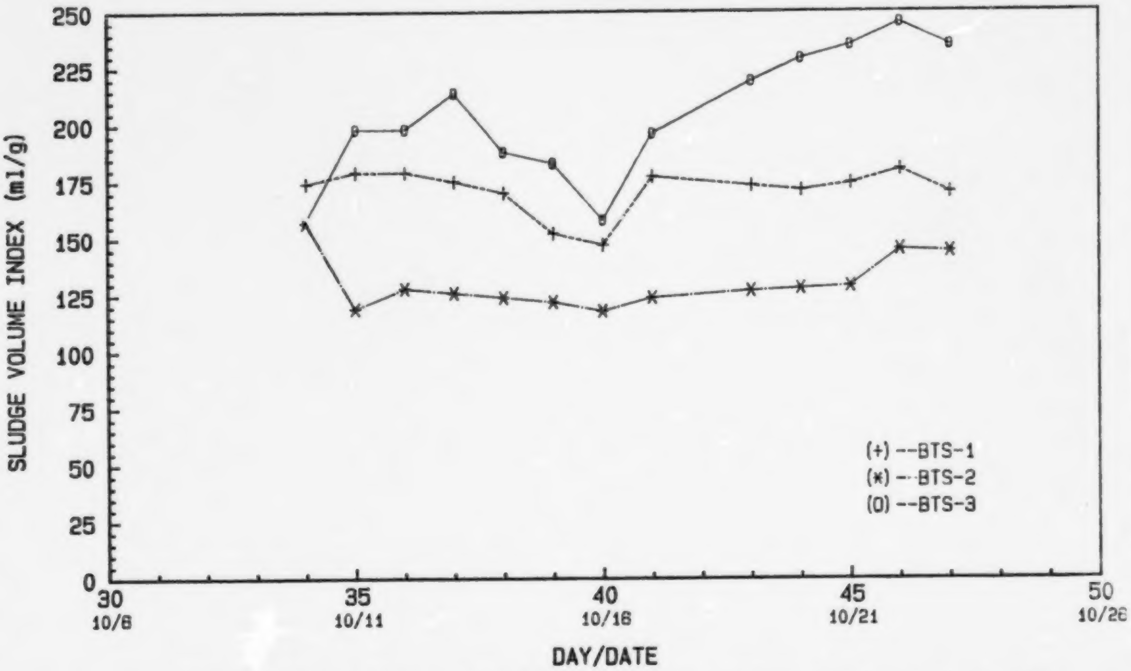


Figure 48. Pilot Plant Sludge Volume Index (SVI) (Day 34-47).

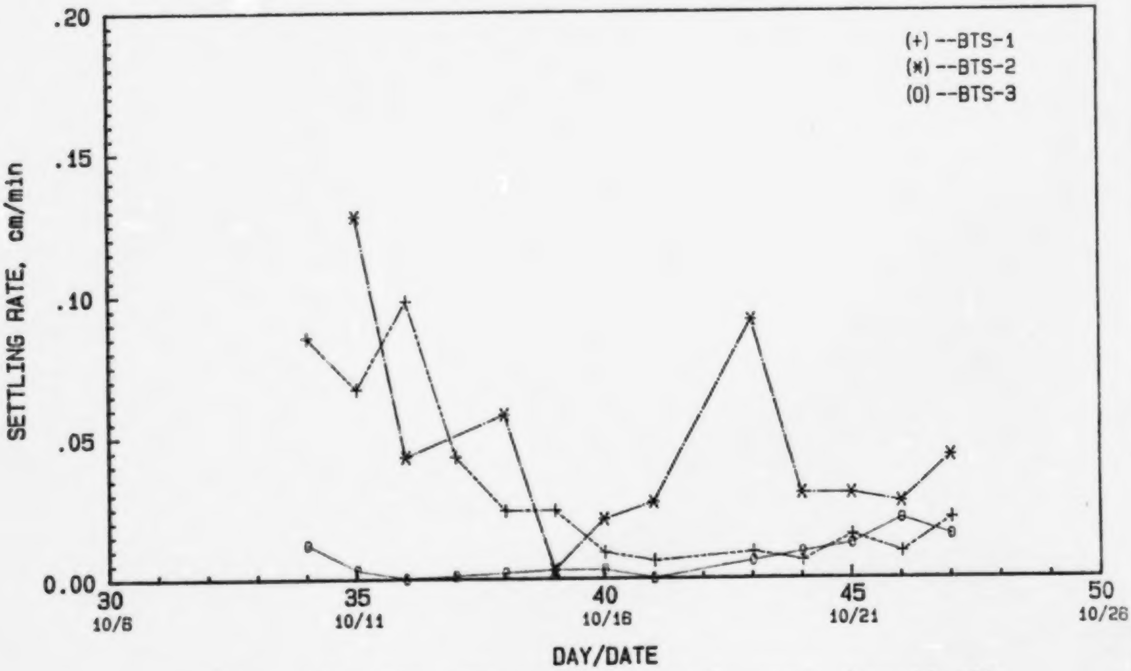


Figure 49. Pilot Plant MLSS Settling Rates (Day 34-47).

Bench settling tests were performed on grab samples (on Oct 24 and 26) of mixed liquor from cell 3 of each pilot unit to evaluate the effect of polymer on MLSS settling. Preliminary jar tests indicated that Percol 763 was effective at dosages of 10 mg/L to 20 mg/L. Percol 726, 727 and 728 were also tested but found to be less effective. Settling tests were performed using dosages of 10 mg/L and 20 mg/L Percol 763. A summary of the bench settling tests is presented in Table 22. The estimated SVI was based on the settled sludge volume after 30 minutes and the composite sample for that day. Settling rate curves are shown on Figures 50 to 52. These curves show that the polymer used was more effective in treating the mixed liquor containing PAC than the control mixed liquor (BTS-3) and most effective in the unit with highest PAC concentration.

Effluent Quality

A summary of the results of analyses of effluent composite samples from each pilot unit during the intensive test phase are listed in Table 21.

The TCOD of the feed wastewater and the effluent from each pilot unit are shown graphically on Figure 40. TCOD, SCOD, TOC and STOC values for the effluent samples from each of the three pilot units are shown on Figures 53 to 55. The effluent TCOD values for all three pilot units during the intensive test phase are shown on Figure 56 and the SCOD values on Figure 57.

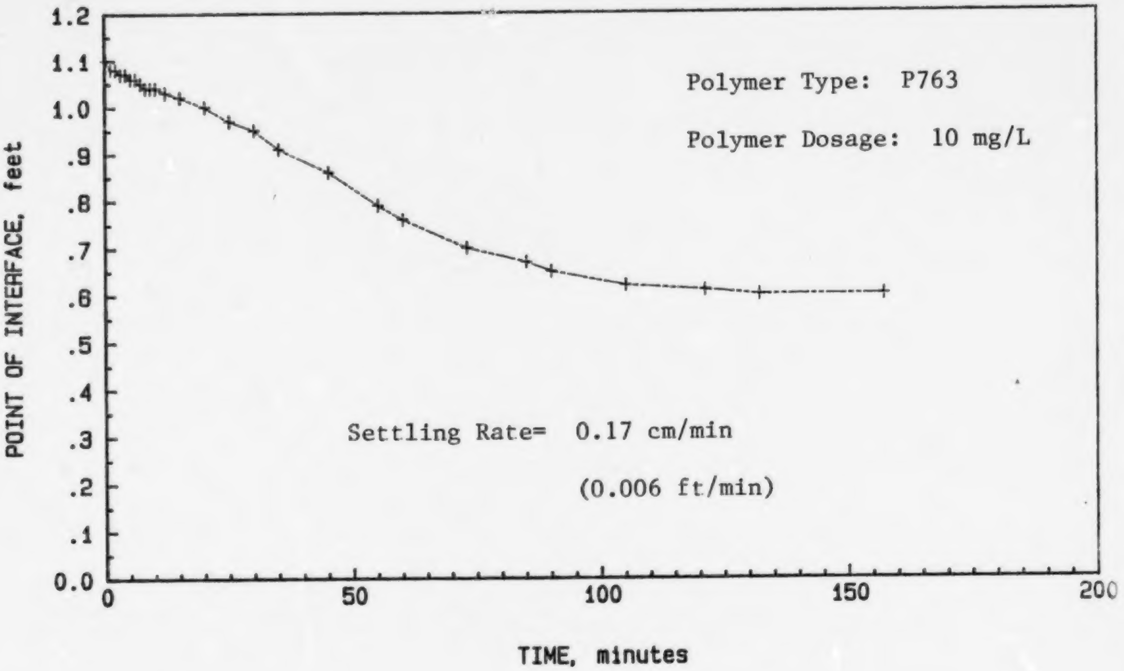
The BTS-1 and BTS-2 effluent TCOD levels were similar during this phase but there was a significant difference in the SCOD concentrations which averaged 459 mg/L and 265 mg/L, respectively. TCOD removals were 92 percent, 93 percent and 86 percent for BTS-1, BTS-2 and BTS-3, respectively,

TABLE 22. BENCH SCALE ML SETTLING TESTS USING POLYMER

UNIT	BTS-1			BTS-2			BTS-3		
Percol 763, mg/L	0	10	20	0	10	20	0	10	20
Rapid Mix time, sec	*	10	10	*	10	10	*	10	10
Flocculation Time, min	*	1	1	*	1	1	*	1	1
Settling Rate, cm/min	0.030	0.17	0.60	0.06	0.56	1.1	0.01	0.09	0.24
Sludge Volume, ml/L									
at 30 min	970	865	590	942	565	460	998	930	795
at 60 min	**	705	470	**	415	385	990	840	620
SVI, ml/g	184	164	112	133	80	65	248	231	198
MLSS, mg/L	5280	5280	5280	7090	7090	7090	4020	4020	4020

* Not applicable.

** No reading was taken at that time.



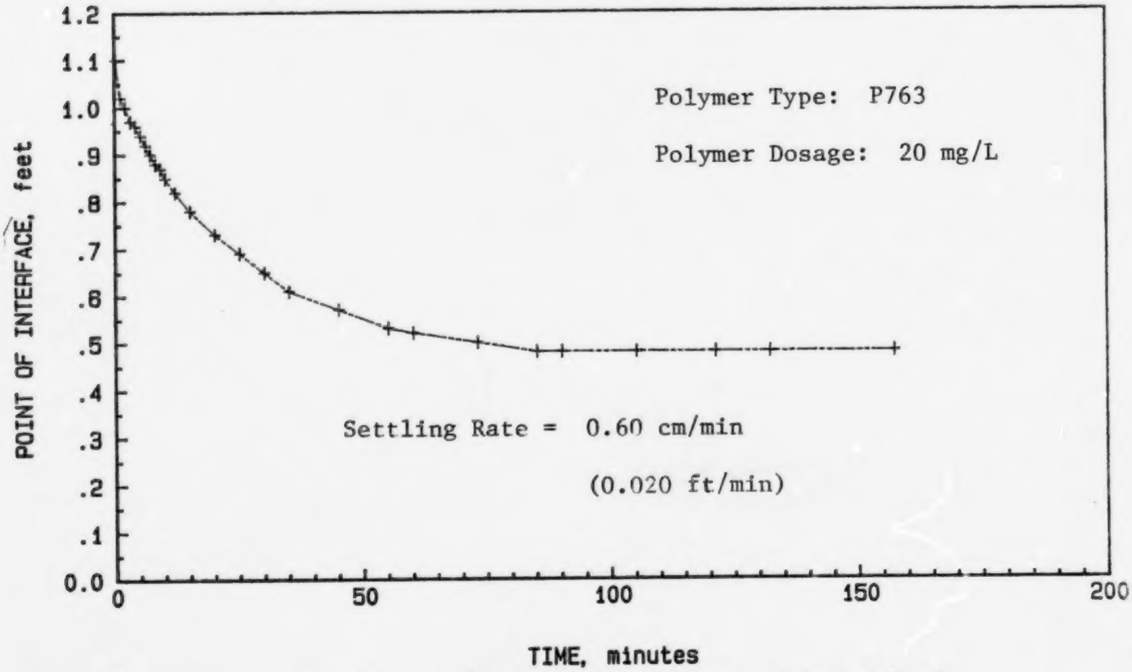
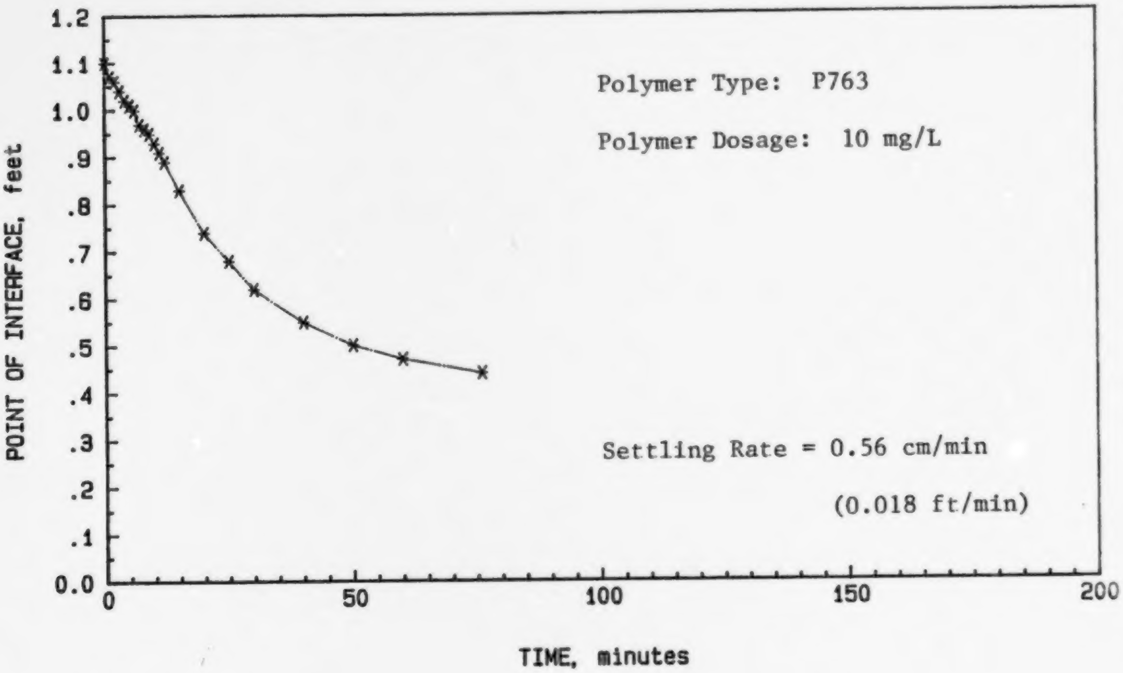


Figure 50. BTS-1, Cell #3 ML Settling Tests with Chemicals (10/24/84).



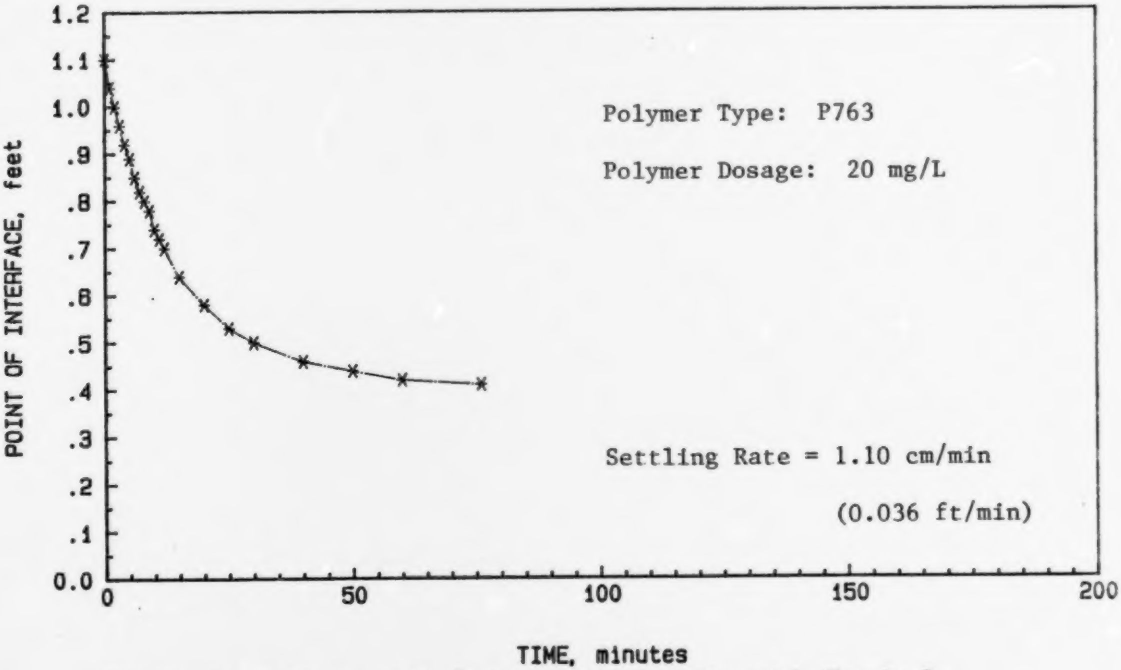
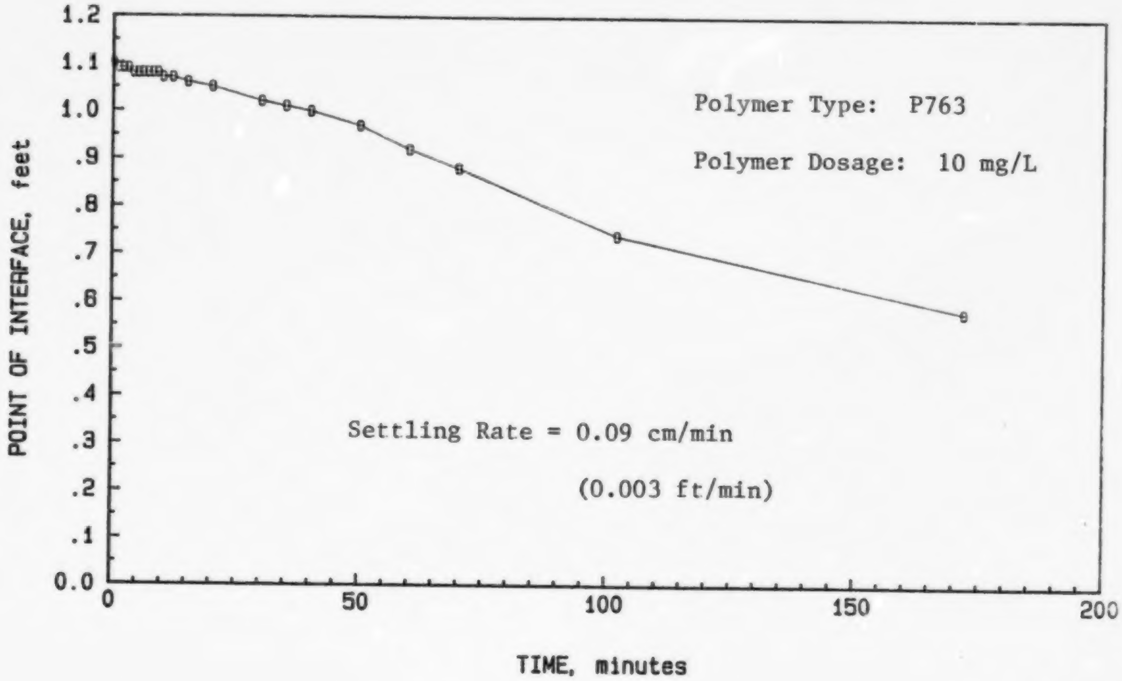


Figure 51. BTS-2, Cell #3 ML Settling Tests with Chemicals (10/24/84).



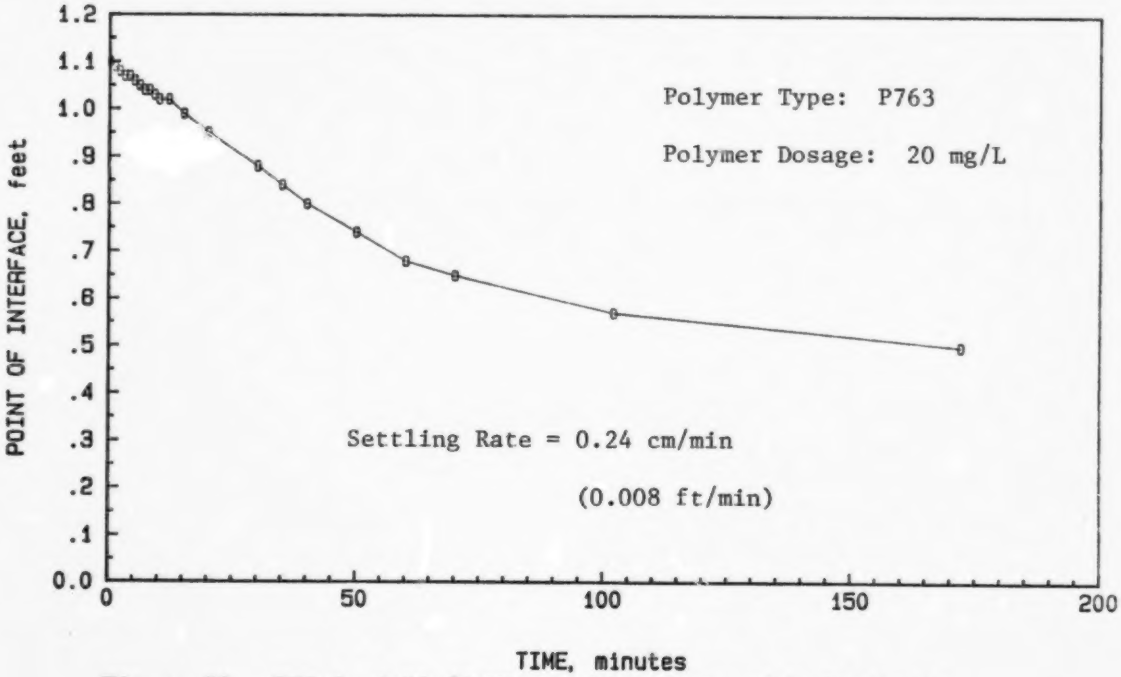


Figure 52. BTS-3, Cell #3 ML Settling Tests with Chemicals (10/26/84).

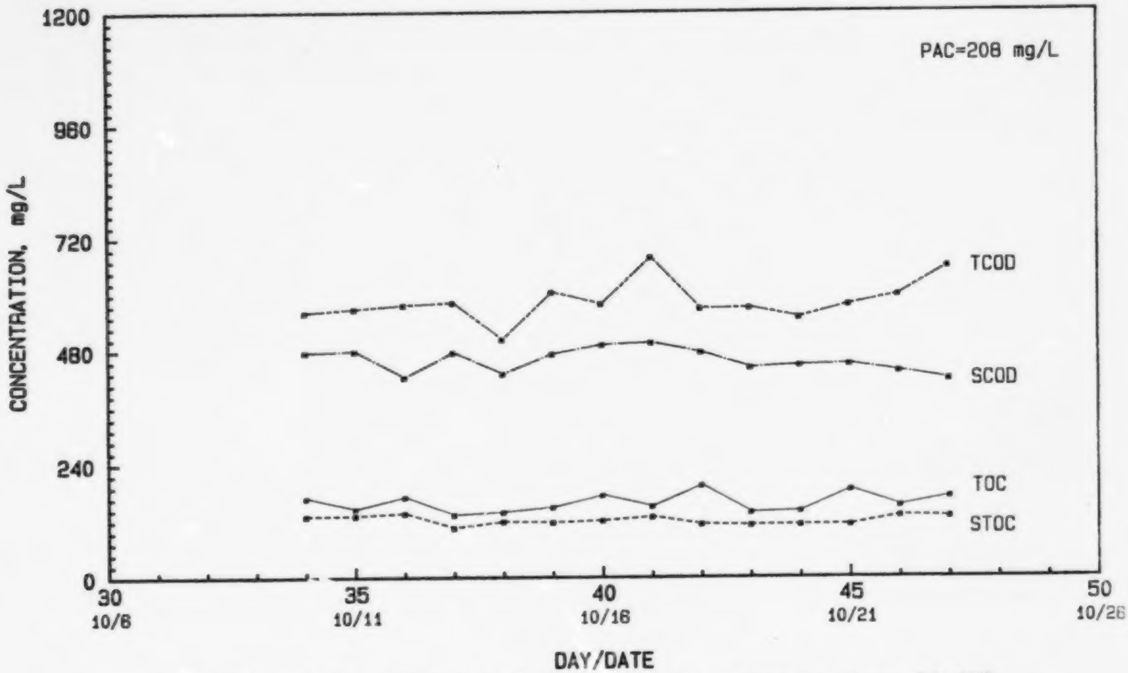


Figure 53. BTS-1 Effluent Organic Content (Day 34-47).

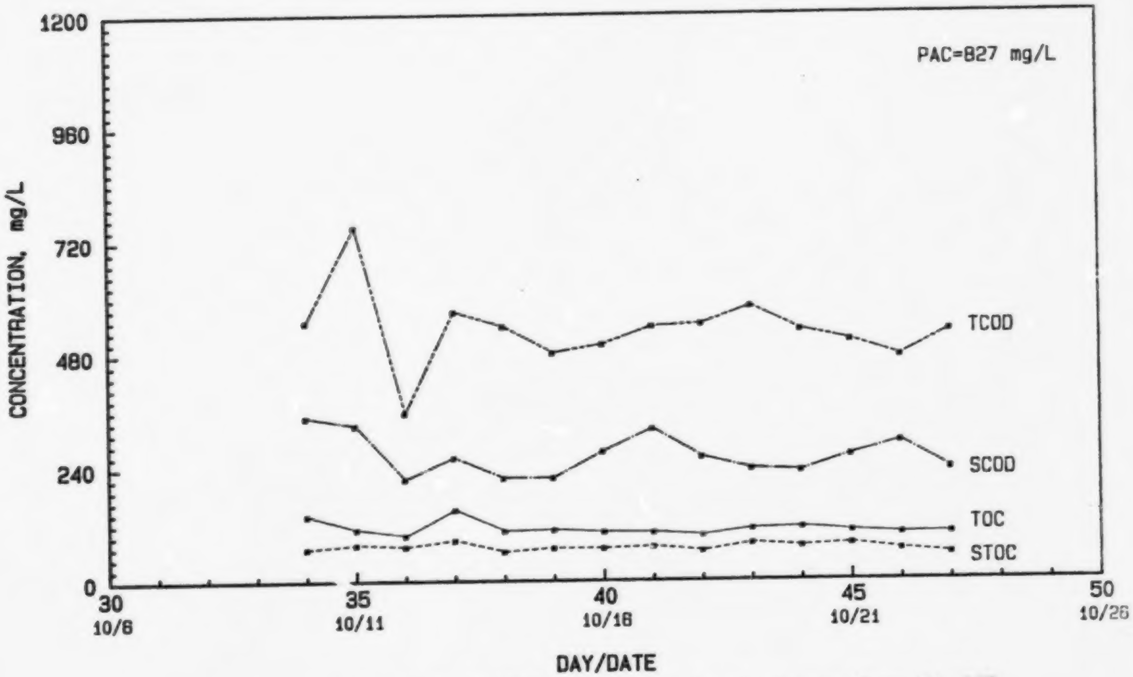


Figure 54. BTS-2 Effluent Organic Content (Day 34-47).

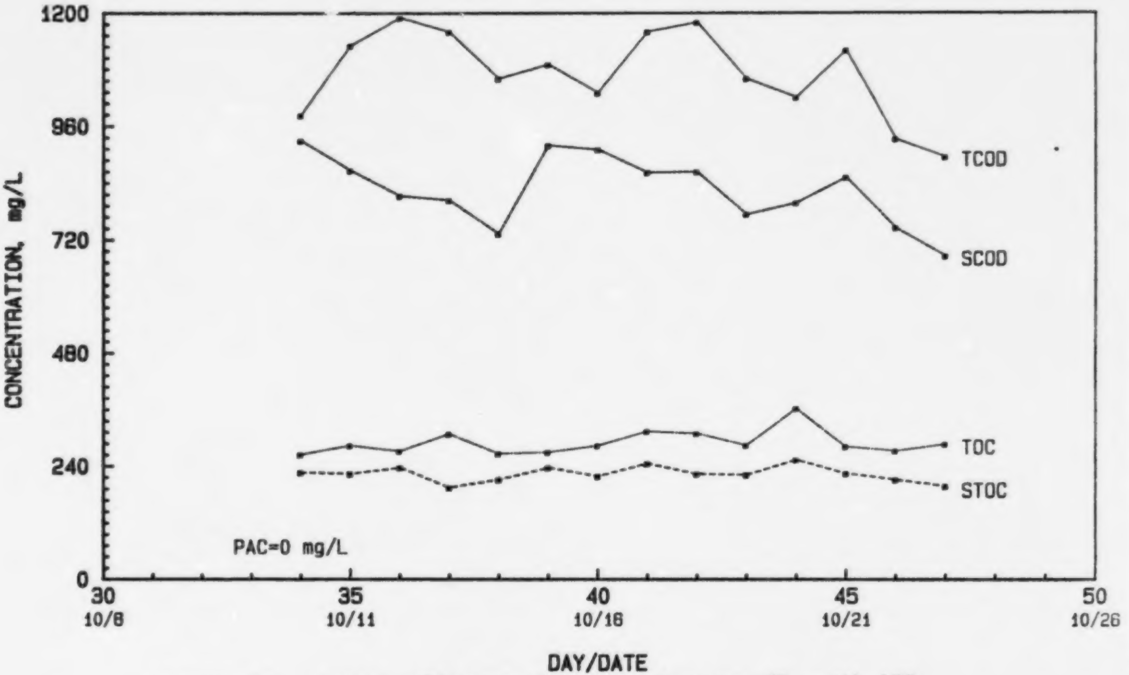


Figure 55. BTS-3 Effluent Organic Content (Day 34-47).

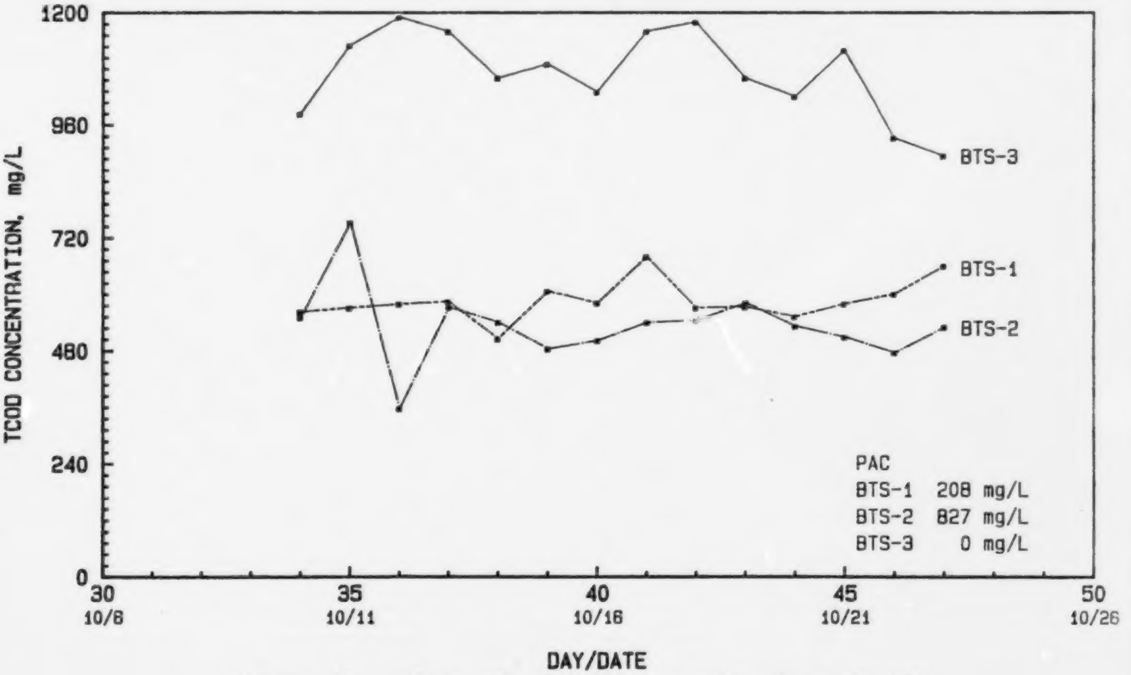


Figure 56. Pilot Plant Effluent TCOD (Day 34-47).

well above the 74 percent BPT average monthly level. The lowest daily TCOD removals measured during this phase were 88 percent, 88 percent and 82 percent for BTS-1, BTS-2 and BTS-3, respectively. TCOD removals during this phase are shown on Figure 58.

Floating solids began to appear on the surface of BTS-2 clarifier on Day 36 and on BTS-1 clarifier a few days later. By Day 42, approximately 2.5 cm of floating scum accumulated on the surface of BTS-1 and BTS-2 clarifiers each day. Gas bubbles were released from the floating scum and gas bubbles were also released from the settled sludge when the clarifier bottoms were scraped. The released gas bubbles, which had no odor, were probably caused by denitrification.

Special daily composite samples of feed wastewater to the biological pilot plants and of effluent from each pilot plant were taken from Day 41 to Day 45 (Oct 17 to Oct 21, 1984). These samples were taken for the identification and measurement of the specific organic compounds resistant to biological treatment. One composite sample was prepared for each sampling point from the daily composite samples. All four composite samples were extracted but only the extract of the BTS-3 composite sample was analyzed because of the complexity of the analyses. The results are presented in Section 10 of this report.

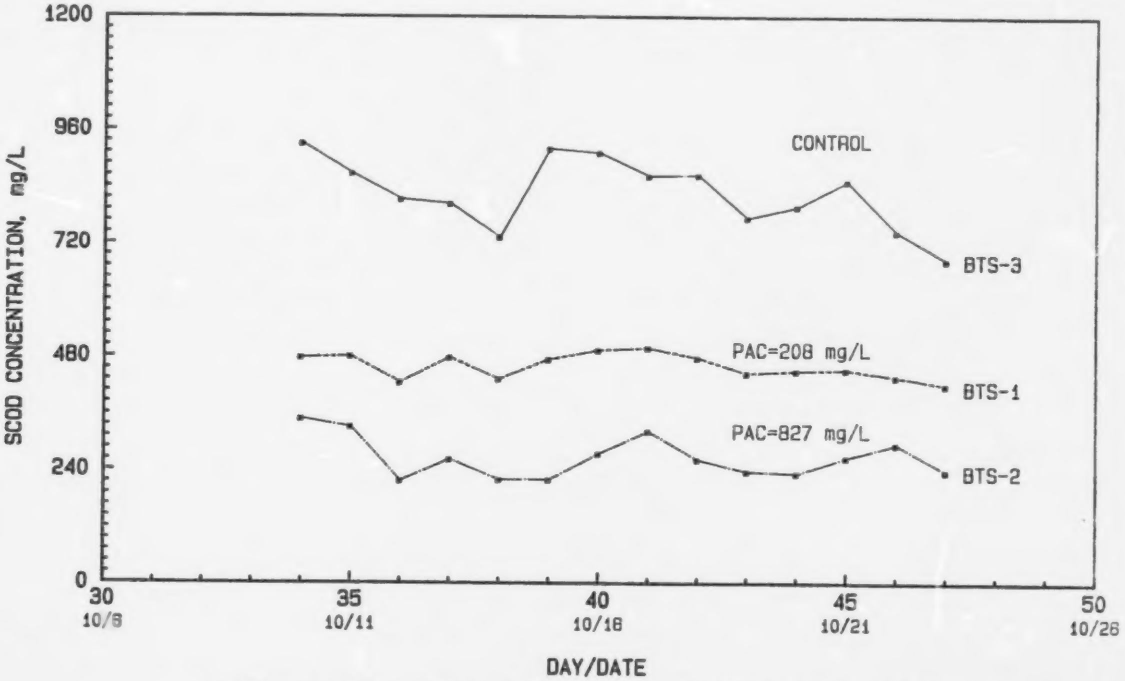


Figure 57. Pilot Plant Effluent SCOD (Day 34-47).

PHASE 4 - SECOND PAC ADDITION AND TRANSITION PERIOD

The PAC dosages to BTS-1 and BTS-2 were increased to 500 mg/L and 1500 mg/L, respectively on October 24, 1984 (Day 48). Additional single doses of carbon were added each day to the aeration basins for ten days to bring the PAC concentration to the expected equilibrium level. The amounts of PAC added as single doses are listed in Table 4.

As noted previously, the mixed liquor pH of BTS-1 and BTS-2 had begun to decrease about a week before the first intensive test period started. The BTS-3 mixed liquor pH started to decrease during the intensive test phase. It was surmised that this gradual drop in pH may have been the result of nitrification in the pilot units. Grab samples of the raw wastewater, the full-scale plant effluent and effluents from each of the pilot plant units were taken on October 27, 1984 (Day 51) for analysis. The samples were preserved with sulfuric acid immediately after collection, iced, and transported to the Rexnord laboratory in Milwaukee the same day. The samples were analyzed for ammonia, total Kjeldahl nitrogen, nitrate and nitrite. The results of these analyses are listed in Table 23. These data confirm that significant nitrification was occurring in the pilot plants. There was no apparent nitrification occurring in the full-scale treatment plant. The pilot plants receiving PAC (BTS-1 and BTS-2) also showed evidence of a significant amount of denitrification.

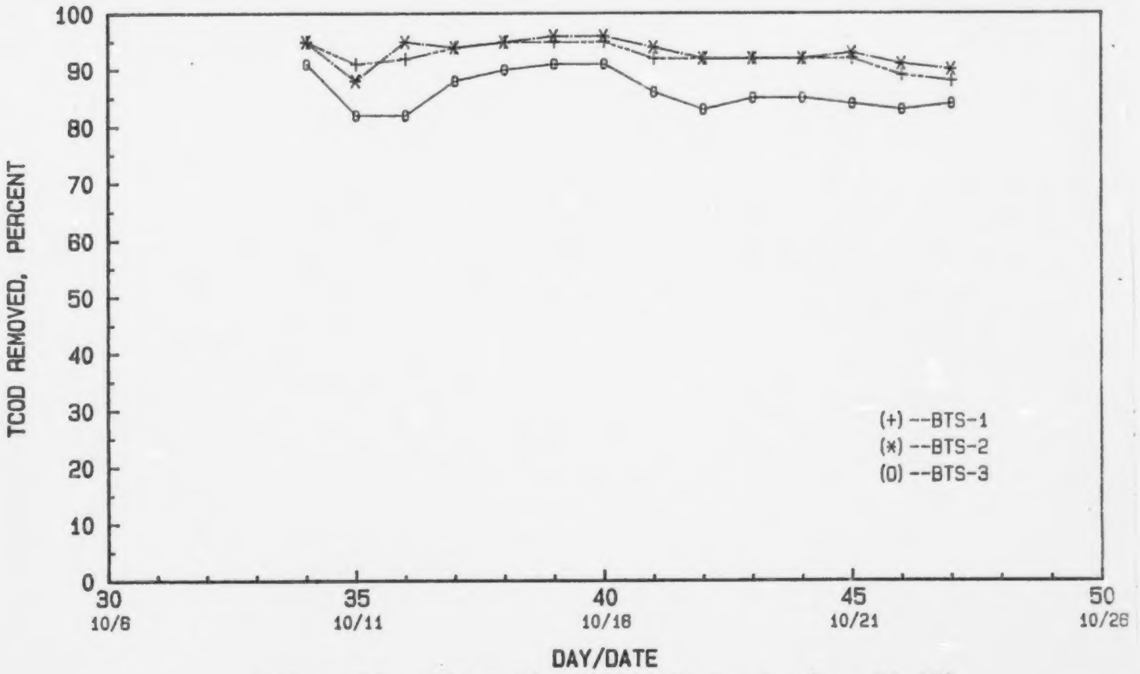


Figure 58. Pilot Plant TCOD Removals (Day 34-47).

It appeared that denitrification (conversion of nitrate to nitrogen gas) occurred in the BTS-1 and BTS-2 clarifier sludge blankets producing nitrogen gas which caused some of the solids to float. Although the control pilot plant (BTS-3) was nitrifying, there was no evidence of denitrification. There was no problem with floating scum in the BTS-3 clarifier and no gas bubbles were released from the sludge blanket during scraping.

The addition of sodium hydroxide to the aeration tanks was started on Day 44 of Phase 3 to try to maintain the mixed liquor pH near 7. Initially, sodium hydroxide was added manually in dilute solutions to raise the pH gradually. On Day 47, continuous addition of sodium hydroxide was initiated and continued during periods of low mixed liquor pH. In addition, large amounts of sodium hydroxide were added manually to each aeration cell on Days 46 and 53 when the feed wastewater was highly acidic for short periods of time. Figures 59 to 61 show the mixed liquor pH values for each pilot plant for the entire study. The periods when sodium hydroxide was added to each unit are indicated on these figures.

Temperatures of all three pilot plants were generally close during this period (Figure 62). On Day 61 the temperature of BTS-3 dropped to a low

TABLE 23. NITROGEN DATA - OCTOBER 27, 1984 (Day 51)

Sample	Feed	Full-Scale Plant Effluent	BTS-3 Effluent	BTS-1 Effluent	BTS-2 Effluent
Sample Point	B	J	F3	F1	F2
System PAC Dosage, mg/L	0	0	0	208	827
Ammonia, mg/L	***	109	27	16	1
TKN, mg/L as N	330	241	55	59	39
Soluble TKN, mg/L as N	316	216	48	53	28
Nitrate, mg/L as N	<1	<1	178	85	87
Nitrite, mg/L as N	<1	<1	<1	<1	<1
Feed TKN in mg/L N Converted* to Biomass N and to N_2 Gas		89	97	186	204
Effluent TSS, mg/L**	***	***	57	39	53

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* Calculated as difference between feed (TKN) and effluent (TKN + nitrate/nitrite N).

** Suspended solids content of daily composite sample.

*** Not measured.

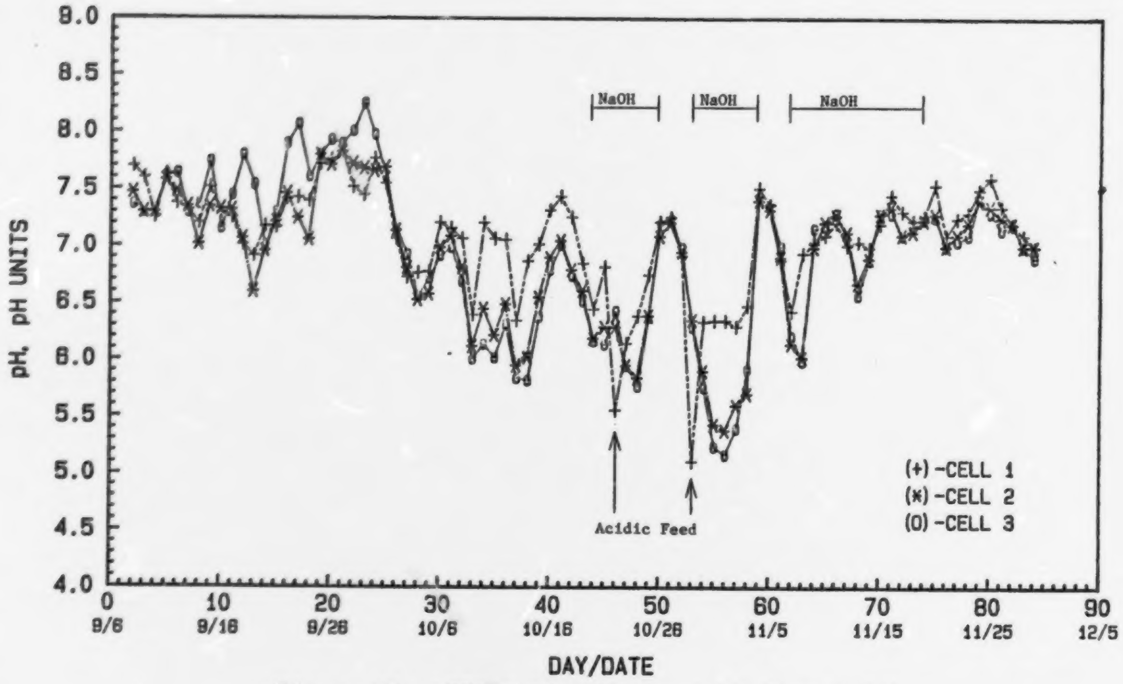


Figure 59. BTS-1 Mixed Liquor pH (Day 1-83).

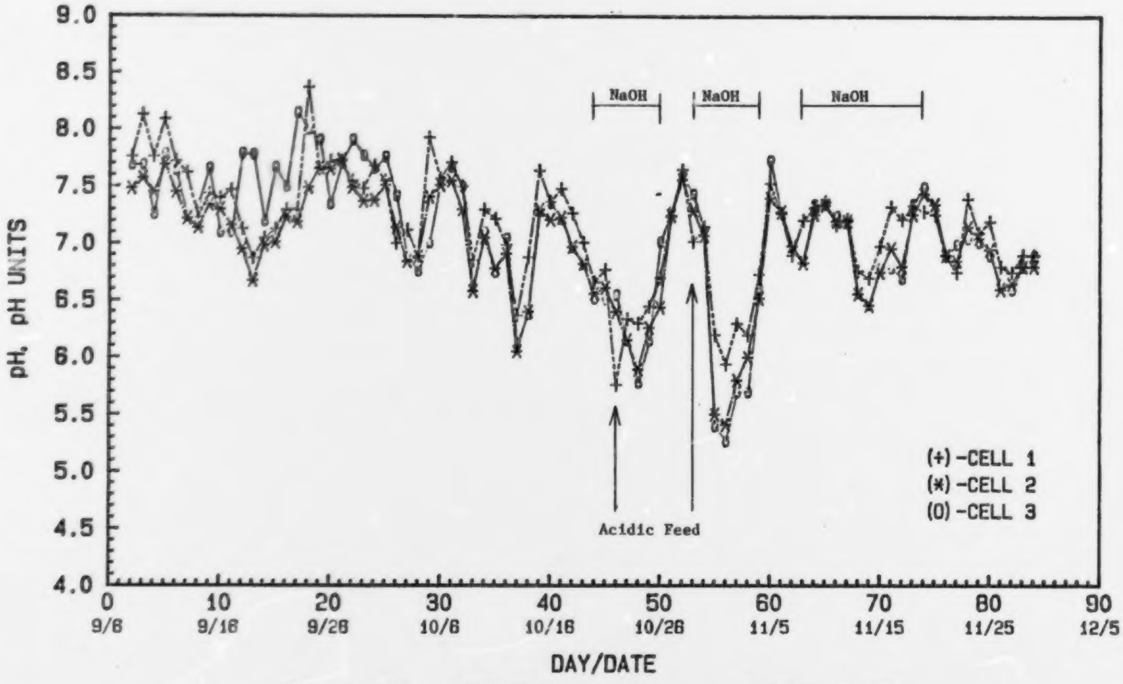


Figure 60. BTS-2 Mixed Liquor pH (Day 1-83).

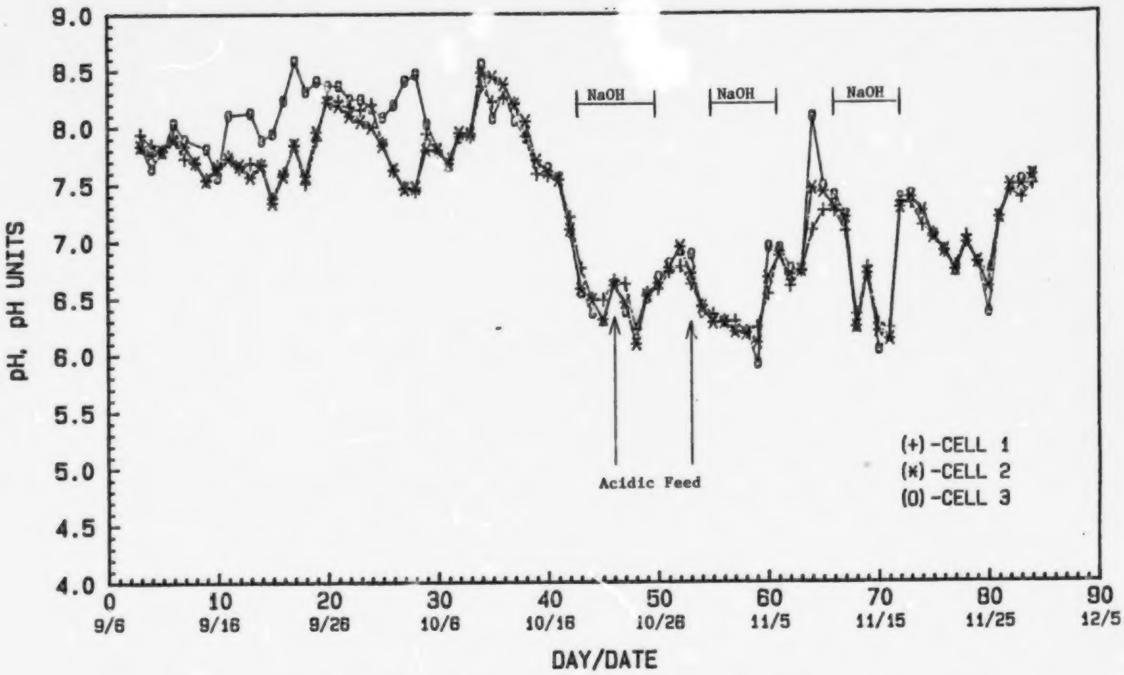


Figure 61. BTS-3 Mixed Liquor pH (Day 1-83).

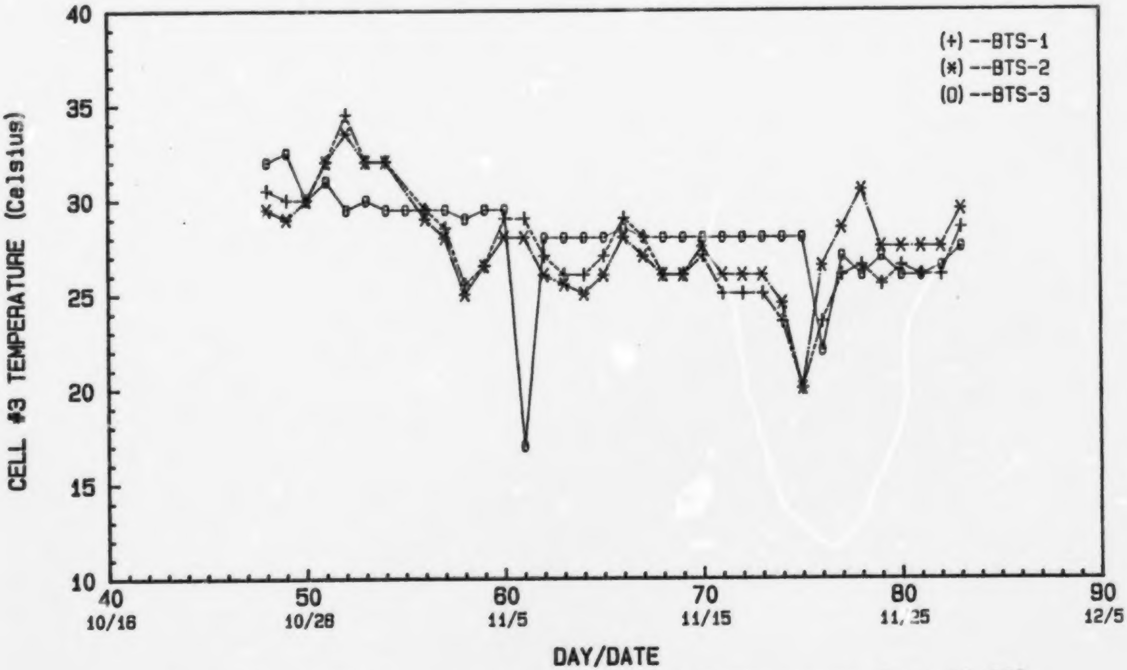


Figure 62. Pilot Plant Aeration Tank Temperature (Day 48-83).

level because of a tripped circuit breaker controlling the aeration tank heaters. On Day 74 and 75, the temperature of BTS-1 and BTS-2 dropped to 20°C because of cold weather. The temperatures soon returned to the normal 26 to 28°C range.

Flows to all three units were controlled to maintain the hydraulic retention time (HRT) at the planned level of three days (Figure 63). Some fluctuation in BTS-3 feed flow occurred from Day 61 to 71 but the average HRT remained about 3 days.

The mixed liquor suspended solids concentrations for each pilot plant from Day 48 to 83 are shown on Figure 64. Shown on this figure is the ten day period when the individual dosages of PAC were added and the periods later selected as representative of system operation in this phase before serious operational problems were encountered. The suspended solids concentration of mixed liquor wasted from the control pilot plant (BTS-3) was relatively uniform for the period. The average mixed liquor suspended solids of 4570 mg/L was similar to the average value of 4790 mg/L for the previous intensive test period (Table 21). Reference to Figure 12 shows that the influent TCOD was also slightly lower than in earlier test phases. The average mixed liquor suspended solids for BTS-1 was 6840 mg/L for the nine days following the completion of the ten day period of extra PAC doses. The problem of floating scum in the clarifier which was first observed during the intensive period became progressively worse during this phase. After the clarifier scum became viscous (Day 66), the scum removed

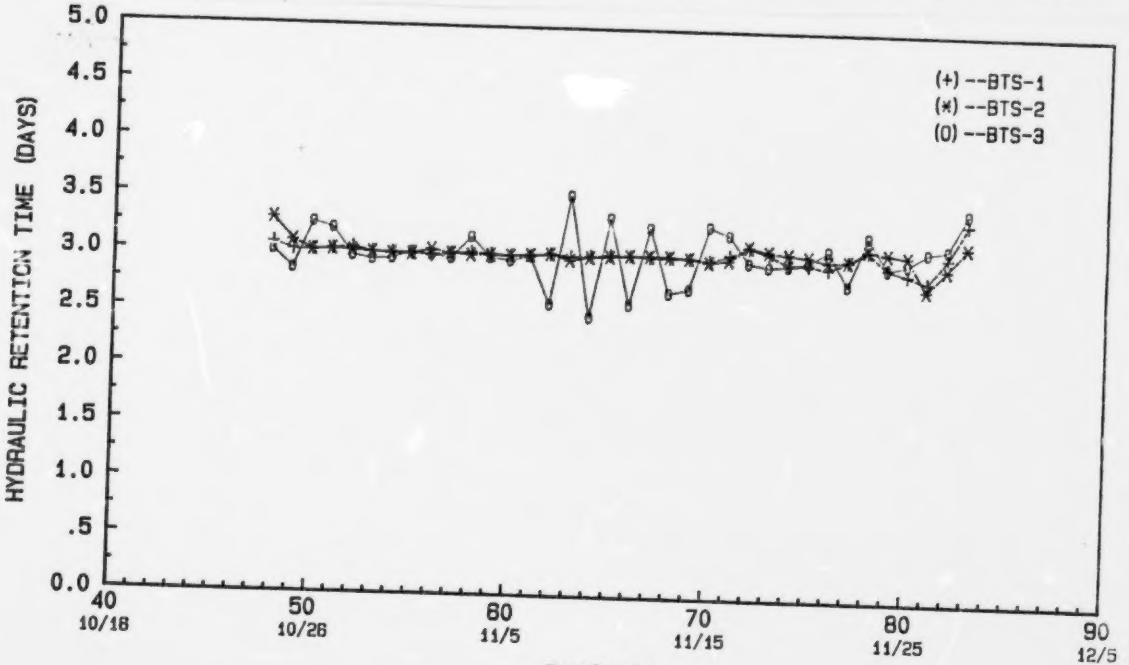


Figure 63. Pilot Plant Hydraulic Retention Time (Day 48-83).

from the clarifier each day was discarded resulting in a gradual decrease in BTS-1 mixed liquor suspended solids.

Partial plugging of the transfer line between the aeration tank and the clarifier of BTS-2 caused the aeration tanks to overflow frequently from Day 56 to 61 resulting in the loss of some solids. The low mixed liquor suspended solids, however, may not be entirely attributed to these overflows. The low suspended solids concentration in BTS-2 effluent indicated that large amounts of solids were not being lost in the effluent. The clarifier sludge blanket did not increase substantially during this period and the thin layer of scum removed from the clarifier each day was recycled to cell 1 of the aeration tank.

Solids retention times during this phase are shown on Figure 65. SRT values for BTS-1 are not shown after Day 68 when wasting of BTS-1 clarifier floating solids was started.

Mixed liquor dissolved oxygen concentrations are shown on Figures 66 to 68. There was no problem keeping the BTS-3 dissolved oxygen concentration above 1 mg/L (Figure 68). Limited blower capacity, however, resulted in low dissolved oxygen levels in BTS-1 and BTS-2 on certain days.

Effluent suspended solids concentrations are shown on Figure 69. The effect of the viscous floating scum in the BTS-1 clarifier on effluent suspended solids is evident. Polymer was added to the BTS-1 mixed liquor entering the clarifier on Day 78. The polymer improved the effluent

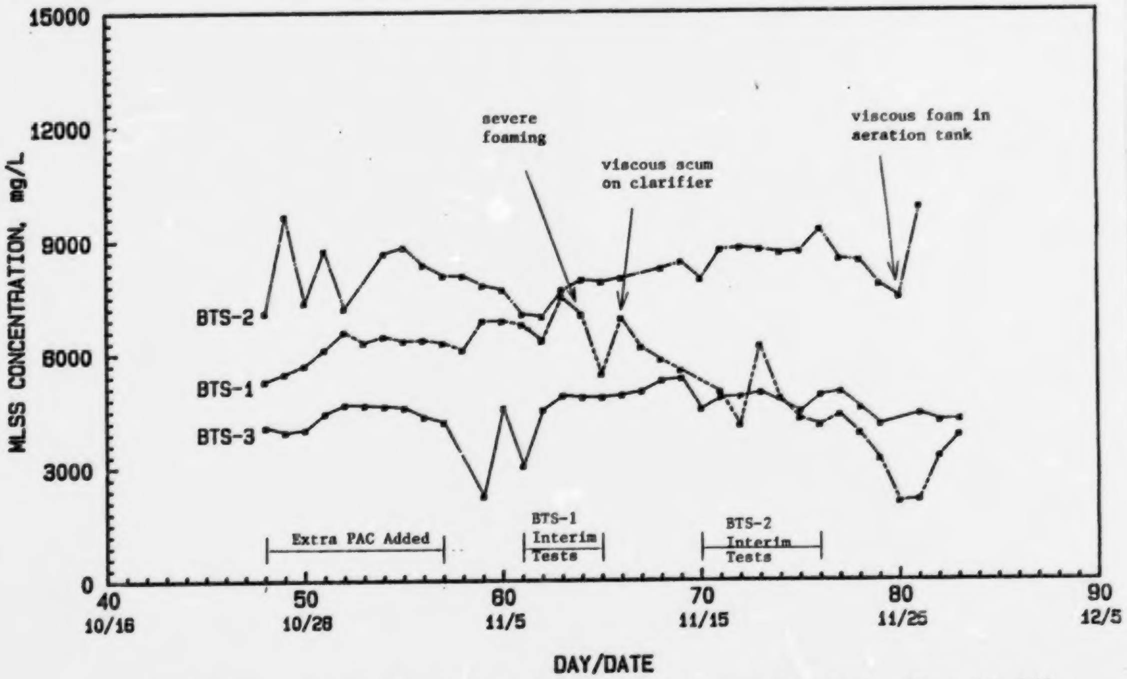


Figure 64. Pilot Plant Mixed Liquor Suspended Solids (Day 48-83).

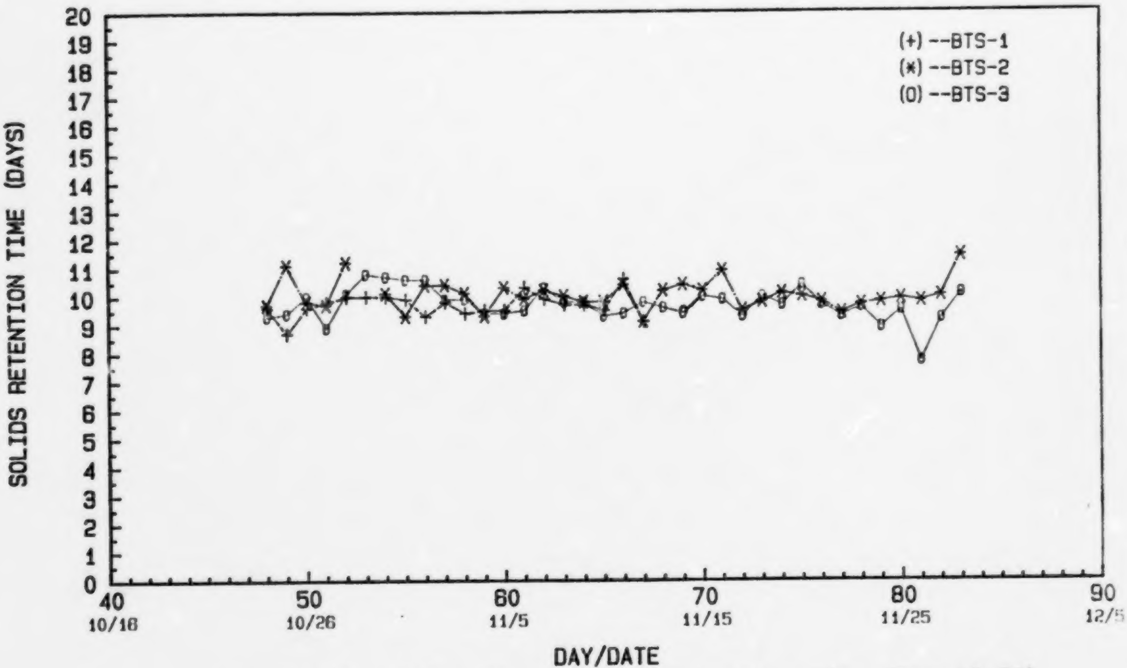


Figure 65. Pilot Plant Solids Retention Time (Day 48-83).

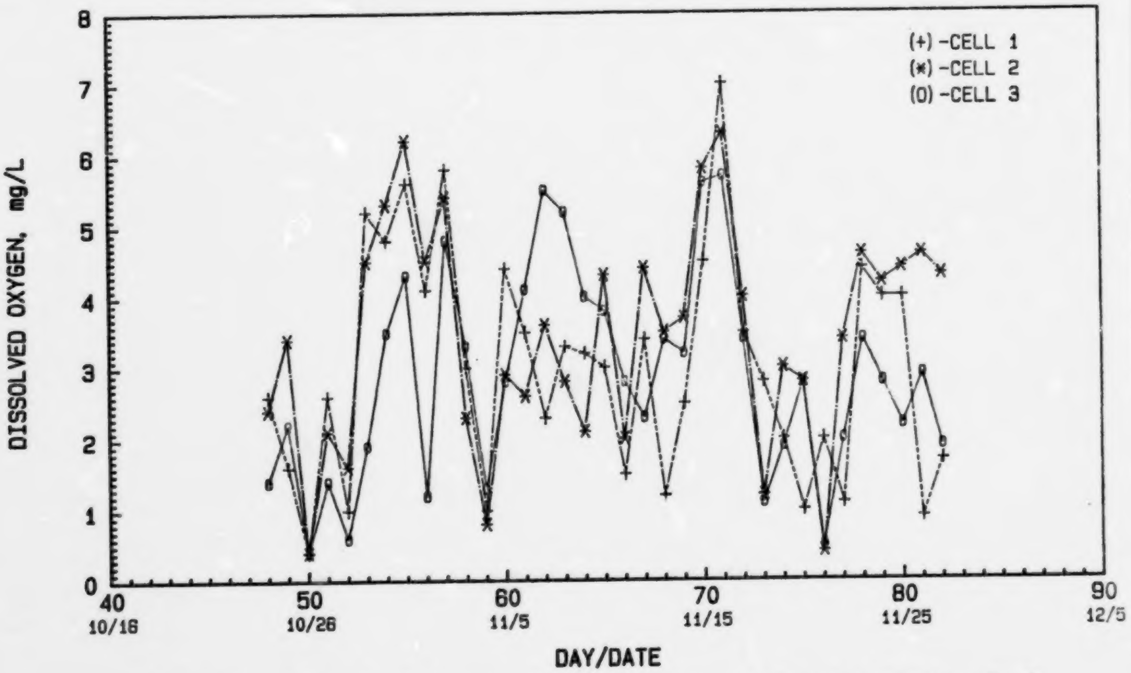


Figure 66. Dissolved Oxygen Concentration in BTS-1 Aeration Tank (Day 48-83).

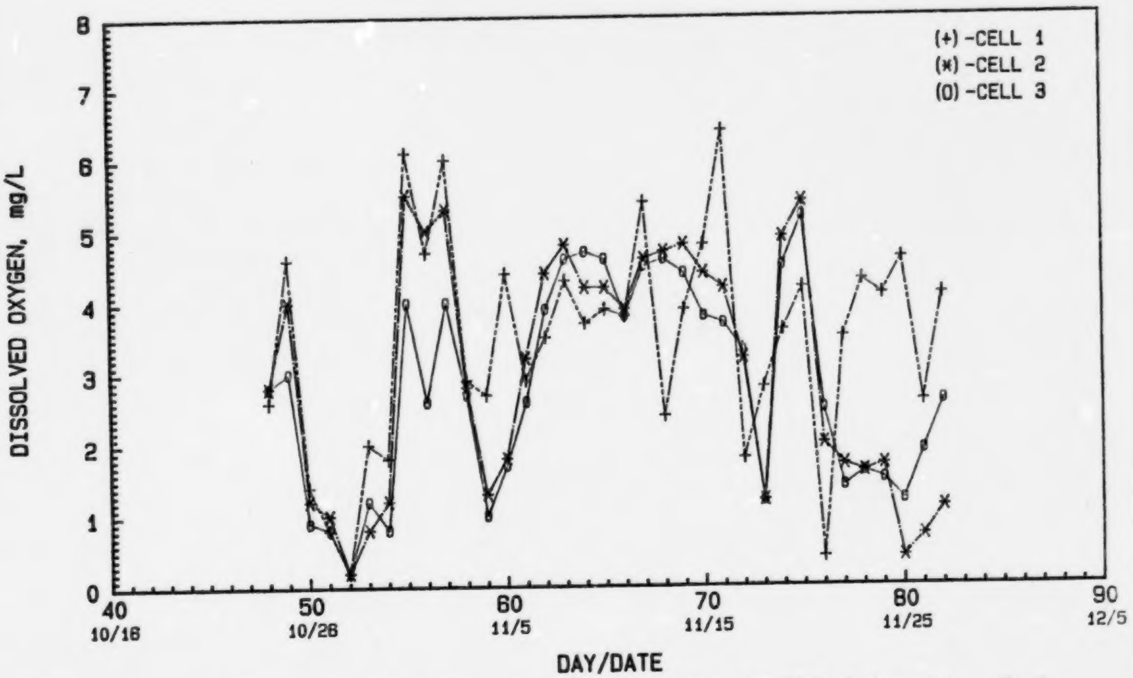


Figure 67. Dissolved Oxygen Concentration in BTS-2 Aeration Tank (Day 48-83).

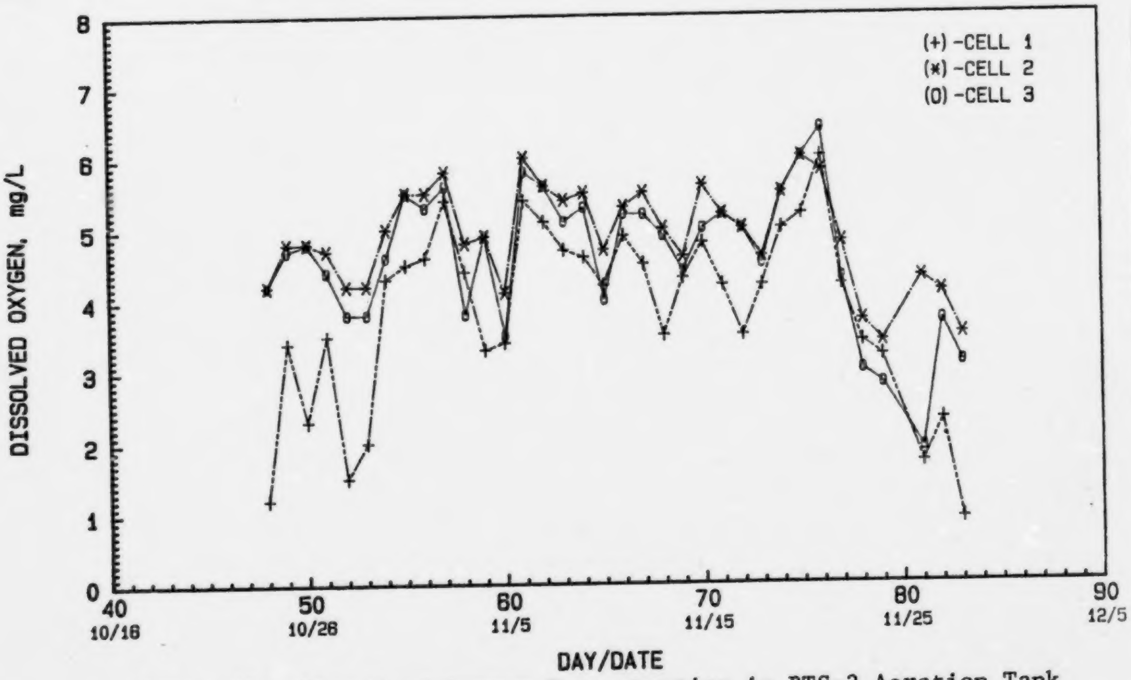


Figure 68. Dissolved Oxygen Concentration in BTS-3 Aeration Tank (Day 48-83).

suspended solids but had no apparent effect on the viscous scum. Although the BTS-2 clarifier scum became similar to the BTS-1 scum by Day 80, the effluent suspended solids did not increase to the same extent before the end of the test.

Influent and effluent TCOD levels for this phase are illustrated on Figure 70. The high TCOD concentrations for BTS-1 effluent between Days 67 and 78 are associated with high effluent suspended solids concentrations. The effect of polymer addition on effluent TCOD level on Day 78 is easily seen. Effluent SCOD concentrations for all three units are shown on Figure 71. In spite of the operational problems in handling the clarifier solids in BTS-1 and BTS-2 and the decrease in BTS-1 mixed liquor suspended solids, the effluent SCOD values were at about the same level at the end of this period as they were at the start of this period.

Operational Problems During Phase 4

Floating mixed liquor solids began to appear on the surface of the BTS-1 and BTS-2 clarifiers during the first intensive test period. This floating mixed liquor solids was probably the result of settled solids floating because of nitrogen gas formed during denitrification. The floating solids were easily broken up and dispersed. The suspended solids had the appearance of normal activated sludge containing PAC. Severe foaming was observed on the surface of the BTS-1 aeration tank on Day 64. On Day 66, it was noticed that the floating mixed liquor solids on the

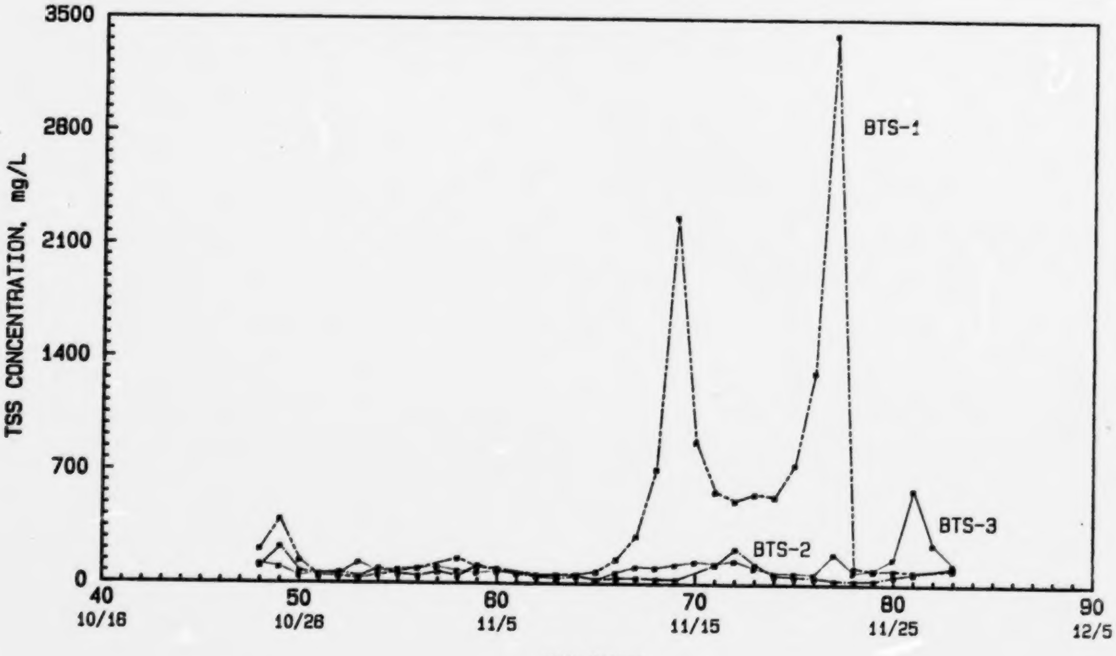


Figure 69. Pilot Plant Effluent Suspended Solids (Day 48-83).

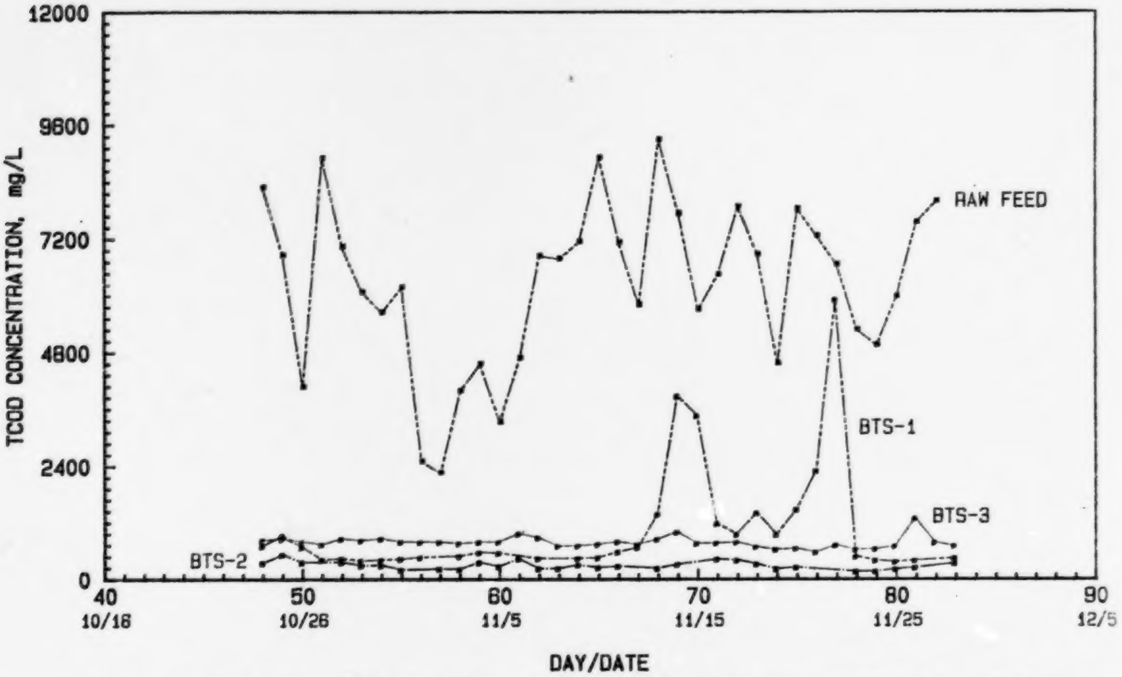


Figure 70. Pilot Plant Influent and Effluent TCOD (Day 48-83).

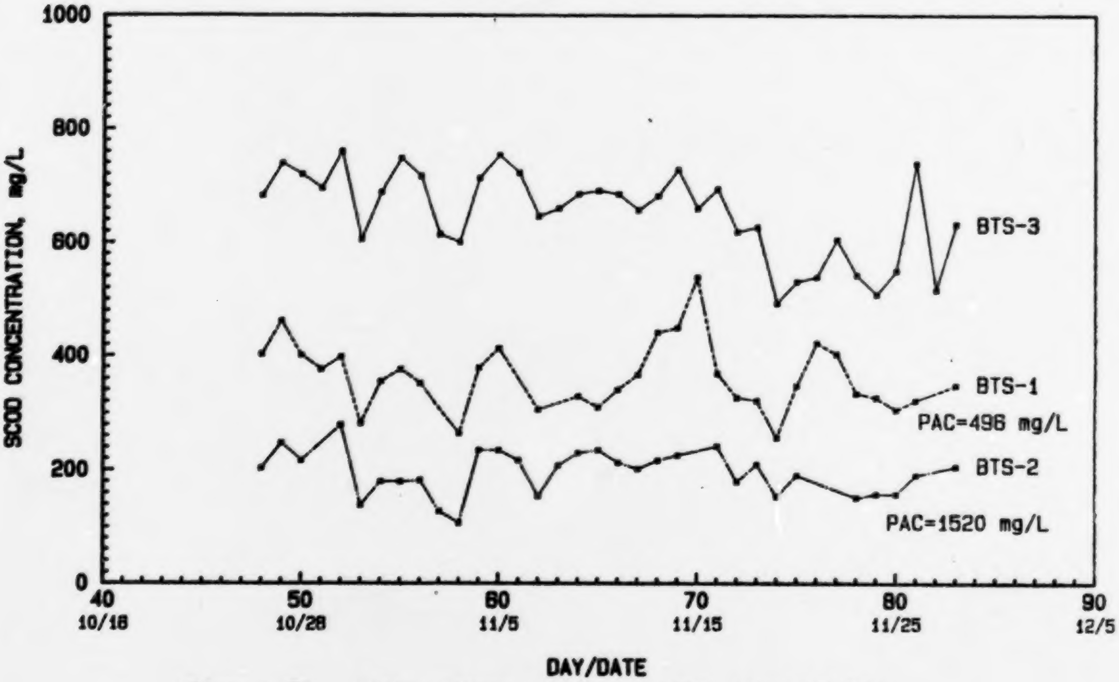


Figure 71. Pilot Plant Effluent SCOD (Day 48-83).

clarifier surface were becoming viscous. Each day the floating solids became more viscous. The viscous floating mixed liquor solids (VFMLS) were difficult to disperse in water but readily adhered to clarifier walls, plastic, glass and skin. Two samples of clarifier VFMLS obtained on Day 70 were analyzed for total solids. They contained 8.8 and 9.1 percent solids, respectively. Starting on Day 69, the VFMLS was removed from the clarifier each day and discarded. Previously, floating solids removed from the clarifier were returned to the aeration tank. Wasting of mixed liquor was discontinued on Day 70 to reduce the loss of MLSS from BTS-1. From 75 to 320 liters of clarifier VFMLS was removed and discarded each day. The mixed liquor suspended solids gradually decreased to about 2,000 mg/L on Day 79. The clarifier VFMLS was again returned to aeration cell 1 of BTS-1 on Days 81 to 83. The effect of wasting the clarifier VFMLS on mixed liquor suspended solids is easily seen on Figure 64. The clarifier sludge blanket became indistinct about Day 70 and was difficult to measure for the remainder of the test.

The floating mixed liquor solids which formed on the BTS-2 clarifier surface each day was not viscous and was easily removed. The floating solids were recycled to cell 1 of the BTS-2 aeration tank. On Day 80, a viscous floating layer of mixed liquor solids began to appear on the surface of cell 2 of the aeration tank. The clarifier floating mixed liquor solids began to become viscous on Day 81. By Day 83 the clarifier VFMLS resembled the VFMLS on BTS-1 clarifier and the VFMLS on the surface of the aeration tank had reached a depth of 15.2 cm in cell 3 and 58.4 cm in cell 2. The VFMLS in cell 2 hindered flow from cell 2 to cell 3 causing overflows from cells 1 and 2. The VFMLS in cell 2 could not be broken up by increasing the air flow to cell 2 or by mechanically mixing the floating blanket. The operational problems caused by the floating VFMLS in the BTS-1 and BTS-2 clarifiers and the floating VFMLS in BTS 2 aeration tank resulted in the cancellation of the second intensive test period (Phase 5). Samples of mixed liquor and clarifier VFMLS were taken for biological examination and the pilot plants were shut down. No evidence of the development of similar viscous floating mixed liquor solids was observed in BTS-3.

Based on observation and prior experience with powdered activated carbon systems, it was postulated that the floating consolidated sludge mass was most likely formed as a result of:

1. Microorganism attachment,
2. Chemical accumulation,
3. Unwetted powdered activated carbon, and/or
4. Oils and grease.

In order to quickly screen the sludge for the above conditions, a set of contact experiments using various solvents was conducted. The following solvents, concentrations, volumes and rationale for choice were used:

1. 450 ml hexane--to dissolve oils and grease,

2. 450 ml 3-percent hydrogen peroxide--to oxidize microorganisms and separate carbon from dead cell material,

3. 450 ml 0.1N nitric acid--to digest microorganisms,

4. 3 ml 15N nitric acid--to digest microorganisms,

5. 450 ml 0.1N sodium hydroxide--to digest microorganisms and solubilize surfactant materials, and

6. 450 ml water--as a control.

Contact with reagents was performed by taking similar portions of unmeasured sludge and placing it into Erlenmeyer flasks containing the individual solvents. The flasks were shaken for 2 hours on a shaker table. Observations were made immediately following contact, approximately 1 hour after shaking and approximately 2 hours after the flasks were removed from the shaker table and allowed to settle.

Similarly, a second set of samples was prepared in test tubes using 20 ml of each solvent. Following contact and observation, the test tube samples were centrifuged for 20 minutes to promote separation (15N nitric acid was not centrifuged).

The following was observed:

1. The hexane had no effect on the sludge at any point of observation; thus, grease agglomeration was not a likely mechanism.

2. Upon addition of the 3-percent hydrogen peroxide, the solution bubbled immediately and dispersed the sludge into fine particles. After shaking for 1 hour, the solution continued to bubble. After settling for approximately 2 hours, the fine particles settled, leaving a portion of larger particles floating. This possibly indicated separation of dead cell material from the carbon.

3. The 0.1N nitric acid had no effect on the sludge. However, the 15N nitric acid broke the sludge up immediately, as did the 0.1N sodium hydroxide solution. Both solvents completely dispersed the sludge after 1 hour of shaking. After the 2-hour settling time a clear water phase and dark carbon/sludge phase existed which indicated possible digestion of microorganisms.

4. When the sample jar of sludge was opened, a strong hydrogen sulfide smell was observed which probably indicated the presence of decaying protein from cell bodies.

5. After centrifuging, floatable material was observed in the 3 percent hydrogen peroxide solution which indicated possible separation of cell material from carbon.

A microscopic examination of untreated sludge was performed but due to the thick density of the sample, no observations of material makeup could be made. No attempt was made to microscopically examine a diluted sample of the untreated sludge. Because standard procedures were followed in wetting the carbon, unwetted powdered activated carbon was unlikely to be the cause of the consolidated sludge mass.

Field efforts to improve dispersions of the VFMLS in water by adjusting pH with sulfuric acid or sodium hydroxide were unsuccessful. Various pH values from less than 1 to 13 were tested. Treatment with a strong hydrogen peroxide solution also was ineffective in improving the water dispersion of the VFMLS.

Grab samples of mixed liquor from each pilot unit, floating VFMLS from the BTS-1 and BTS-2 clarifiers and one sample of floating VFMLS from cell 2 of the BTS-2 aeration tank were obtained and sent to Dr. David Jenkins of David Jenkins and Associates of Kensington, California for biological examination. The complete report of this examination is in Appendix E. A summary of his conclusions concerning the pilot plant operation follows:

1. There was no evidence of extracellular polymeric material by India Ink reverse staining.

2. The relative abundance and type of organisms was similar for all samples from a particular pilot plant unit.

3. Filamentous organism abundance was sufficient to impair settling by floc bridging in BTS-1 and BTS-2 and by floc bridging and open floc structure in BTS-3. The BTS-2 mixed liquor contained the highest concentration of filamentous organisms.

4. The filamentous organisms in BTS-1 and BTS-2 mixed liquors were similar. Type 021N and *H. hydrossis* were abundant in all samples from BTS-1. Type 021N was present in excessive amounts and *H. hydrossis* was abundant in the BTS-2 samples. *H. hydrossis* was abundant in BTS-3 mixed liquor but only a few organisms of Type 021N were found.

Type 021N is often associated with wastewaters that are nutrient deficient or contain high concentrations of soluble organics treated in well-mixed continuous feed systems. *H. hydrossis* occurs at low F/M ratios under moderate dissolved oxygen deficiency.

Photomicrographs of the mixed liquor samples examined by Dr. Jenkins are shown on Figures 72 to 78. Photographs of the mixed liquor from each unit are shown on Figures 72 to 74. The powdered activated carbon particles in the BTS-1 and BTS-2 mixed liquors are evident on Figures 72 and 73. Figures 75 to 78 show examples of *H. hydrossis* and Type 021N organisms found in these mixed liquor samples.

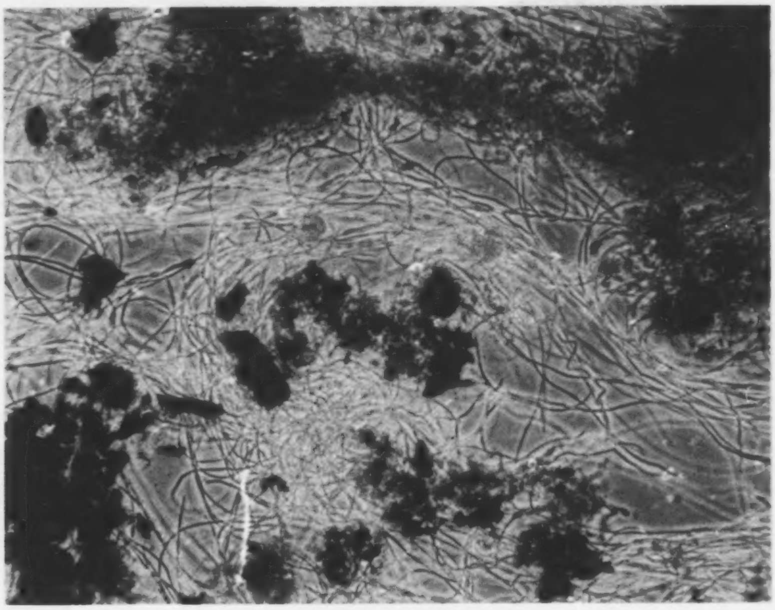


Figure 72. BTS-1 Mixed Liquor (Nov. 29, 1984) 100x magnification.

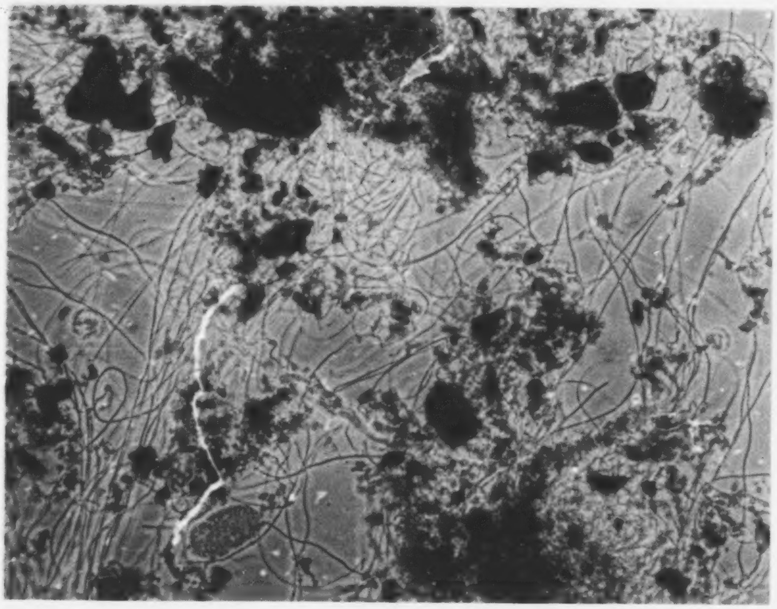


Figure 73. BTS-2 Mixed Liquor (Nov. 29, 1984) 100x magnification.

Figure 74. BTS-3 Mixed Liquor (Nov. 29, 1984) 100x magnification.

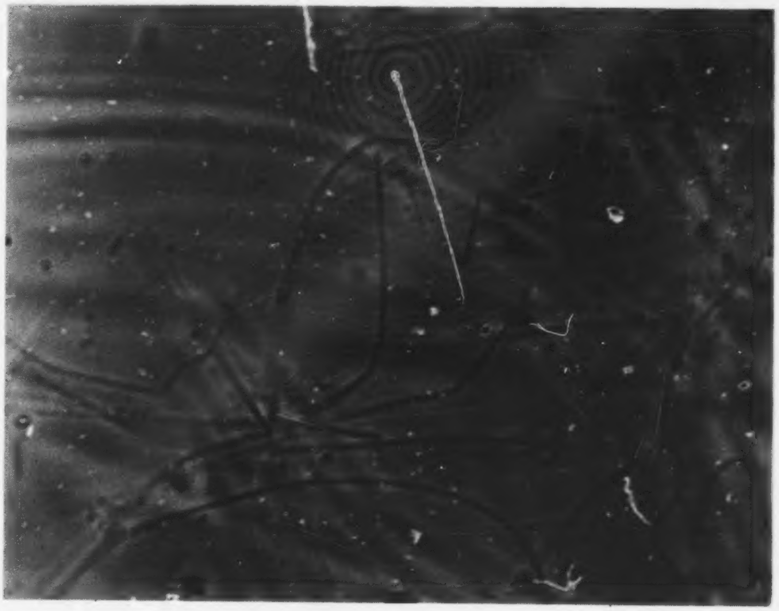


Figure 75. H. hydrossis in BTS-1 ML. 1000x magnification.

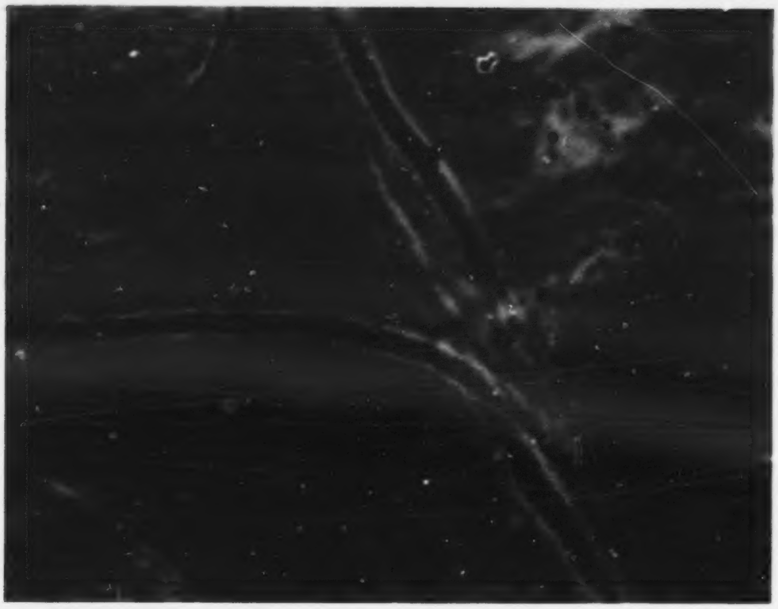


Figure 76. Type 021N in BTS-1 ML. 1000x magnification.

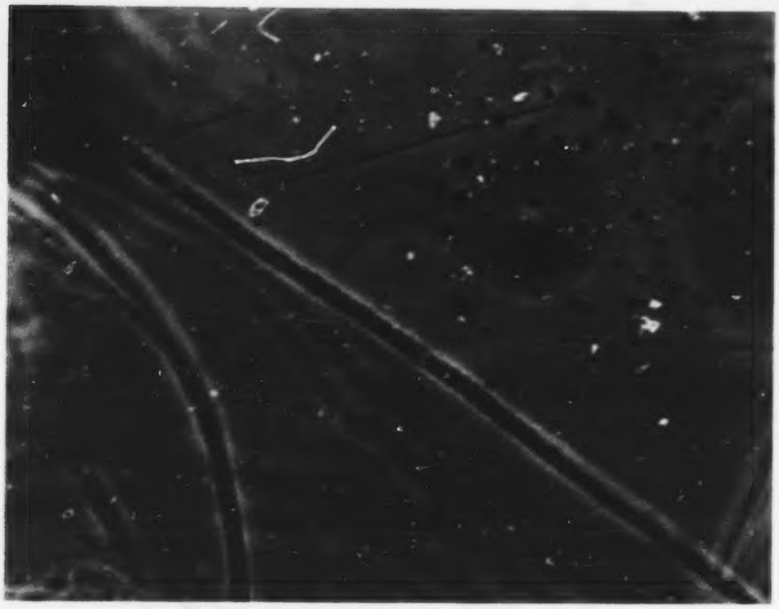


Figure 77. Type 021N in BTS-2 ML. 1000x magnification.

The available nutrient balance data (Table 17) and the examination of the mixed liquor by Dr. Jenkins indicates that nutrient deficiency was probably not the cause of the high concentrations of Type 021N organisms. Dr. Jenkins stated "Type 021N has been associated with nutrient (N and P) deficiency (not in this case based on its morphological appearance and N and P data provided by you); and with well-mixed, continuous-fed activated sludge treating soluble organics (? particularly fatty acids). This may be a possibility in your case since although your units have 3 compartments they have long hydraulic detention times which will allow significant influent dispersion". The feed wastewater did contain high concentrations of soluble organics as indicated by the high average influent TCOD of 7060 mg/L (Table 16). Since the soluble organic concentration in the feed was the same for all pilot plant units, it appears that the presence of PAC in BTS-1 and BTS-2 enhanced the growth of Type 021N.

Samples of feed and effluent from each unit were analyzed for ammonia nitrogen, total Kjeldahl nitrogen and nitrate-nitrite nitrogen during the period when the viscous solids developed. These data, plus similar data obtained during the intensive test period, are presented in Table 24 and show that nitrification continued in all pilot units until Day 83. Some denitrification occurred in both units containing PAC but the amount of denitrification in BTS-2 decreased in the last days of testing.

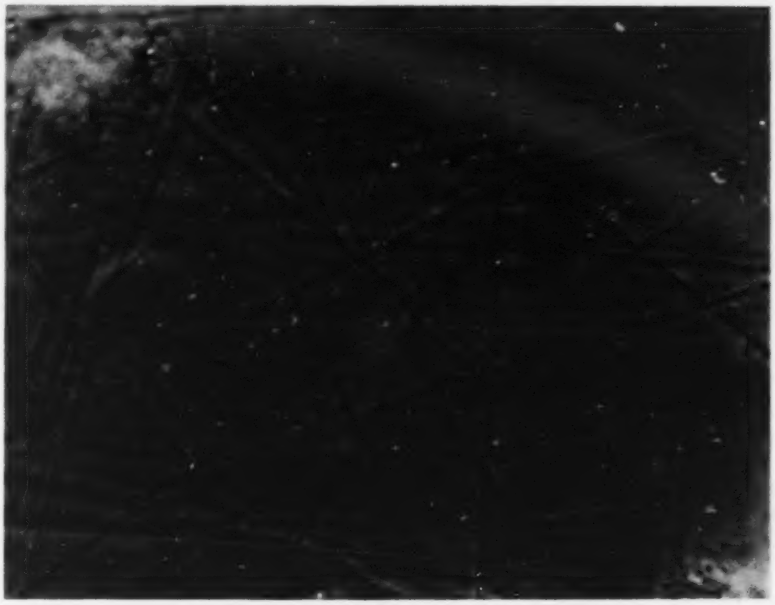


Figure 78. H. hydrossis in BTS-3 ML. 1000x magnification.

Interim Test Periods for BTS-1 and BTS-2

As a result of the viscous floating mixed liquor solids problems in BTS-1 and BTS-2, Phase 5 was cancelled. In spite of this, some information regarding the effect of PAC dosages of 496 and 1520 mg/L was obtained by examining the data from Days 62-65 (November 7-10) for BTS-1 and BTS-3 and from Days 71-76 (November 16-21) for BTS-2 and BTS-3. These were periods of relatively stable operation just before the appearance of the VFMLS in each pilot plant.

TABLE 24. PILOT PLANT NITROGEN DATA

Day	Date	Sample Site	PAC Dosage (mg/L)	Total Kjeldahl Nitrogen (mg/L as N)	Ammonia Nitrogen (mg/L as N)	Nitrate Nitrite Nitrogen (mg/L as N)
51	10/27/84	Feed (B)	0	316	*	<1
51	10/27/84	Full-Scale Eff (J)	0	216	109	<1
51	10/27/84	BTS-3 Eff (F3)	0	55	27	178
51	10/27/84	BTS-1 Eff (F1)	208	59	16	85
51	10/27/84	BTS-2 Eff (F2)	827	39	1	87
70	11/15/84	Feed (B)	0	300	250	3.2
70	11/15/84	BTS-3 Eff (F3)	0	28	7.4	189
70	11/15/84	BTS-1 Eff (F1)	496	39	3.4	73
70	11/15/84	BTS-2 Eff (F2)	1520	11	2.3	111
74	11/19/84	Feed (B)	0	130	65	1.8
74	11/19/84	BTS-3 Eff (F3)	0	25	1.1	174
74	11/19/84	BTS-1 Eff (F1)	496	33	3.9	29
74	11/19/84	BTS-2 Eff (F2)	1520	7.3	1.3	70
80	11/25/84	Feed (B)	0	380	92	3.4
80	11/25/84	BTS-3 Eff (F3)	0	*	3.8	163
80	11/25/84	BTS-1 Eff (F1)	496	*	7.8	38
80	11/25/84	BTS-2 Eff (F2)	1520	*	2.3	102
82	11/27/84	Feed (B)	0	410	80	3.6
82	11/27/84	BTS-3 (F3)	0	76	9.9	145
82	11/27/84	BTS-1 (F1)	496	*	*	*
82	11/27/84	BTS-2 (F2)	1520	*	*	*
83	11/28/84	Feed (B)	0	180	51	2.8
83	11/28/84	BTS-3 Eff (F3)	0	46	4.3	137
83	11/28/84	BTS-1 Eff (F1)	496	31	8.3	48
83	11/28/84	BTS-2 Eff (F2)	1520	20	1.4	92

* Analysis was not performed.

BTS-1 Interim Test Period

A summary of the operation of the BTS-1 and BTS-3 pilot plants during the BTS-1 interim test period is presented in Table 25. The hydraulic and solids retention times were very close to the planned values of 3 and 10 days, respectively. The aeration tank temperatures of both pilot plant units were similar but about five degrees lower than during the first intensive test period. The continuous addition of sodium hydroxide to cell 3 of each pilot unit, which had been stopped 2 days earlier, was resumed on Day 62. The aeration tank pH values of each unit are shown on Figures 79 and 80. All mixed liquor dissolved oxygen concentrations were greater than

TABLE 25. SUMMARY OF BIOLOGICAL PILOT PLANT OPERATION INTERIM TEST PERIOD FOR BTS-1 (DAY 62-65, NOV 7-10, 1984)

	BTS-1		BTS- 3	
Parameter	Average (n)	Range	Average (n)	Range
Operation Data				
Feed Flow, L/min	1.38 (4)	1.37-1.38	0.045 (4)	0.037-0.053
PAC Flow, ml/min	31 (4)	30-33	*	
RS Flow, L/min	3.80 (4)	3.45-4.22	0.092 (4)	0.09-0.093
RS Flow, % of Feed	275 (4)	252-306	204 (4)	175-243
Waste ML Flow, ml/min	419 (4)	411-425	13 (4)	12-14
PAC Dosage, mg/L	496 (4)	482-522	0	
F/M, g TCOD/day-g MLSS	**	**	0.69 (1)	-##
HRT, days	3.0 (4)	3.0-3.0	3.0-3.0	2.5-3.5
SRT, days	9.7 (4)	9.5-9.9	9.8-(4)	9.3-10.3
Mixed Liquor Data				
Temp, °C	27 (12)	26-27	28 (12)	28-28
pH	***	6.0-7.2	***	6.6-8.1
DO, mg/L	3.6 (12)	2.3-5.5	5.0 (12)	4.0-5.6
TSS, mg/L	7000 (4)	6340-7480	4770 (4)	4520-4880
SVI, ml/g	142 (3)	132-155	206 (3)	198-215
Settling Rate, cm/min	0.015 (3)	0.009-0.018	0.036 (3)	0.027-0.040
Effluent Data				
TCOD, mg/L	454 (3)	446-464	770 (4)	712-894
SCOD, mg/L	314 (3)	305-328	670 (4)	645-690
TOC, mg/L	115 (2)	112-118	#	#
TSS, mg/L	59 (3)	50-73	44 (4)	23-55
VSS, mg/L	50 (1)	-##	46 (1)	-##

*PAC not added to BTS-3.
**F/M ratios not calculated for BTS-1 because of PAC in MLSS.
***Average pH values not calculated.
#No measurements of this parameter during this test period.
##Only one value

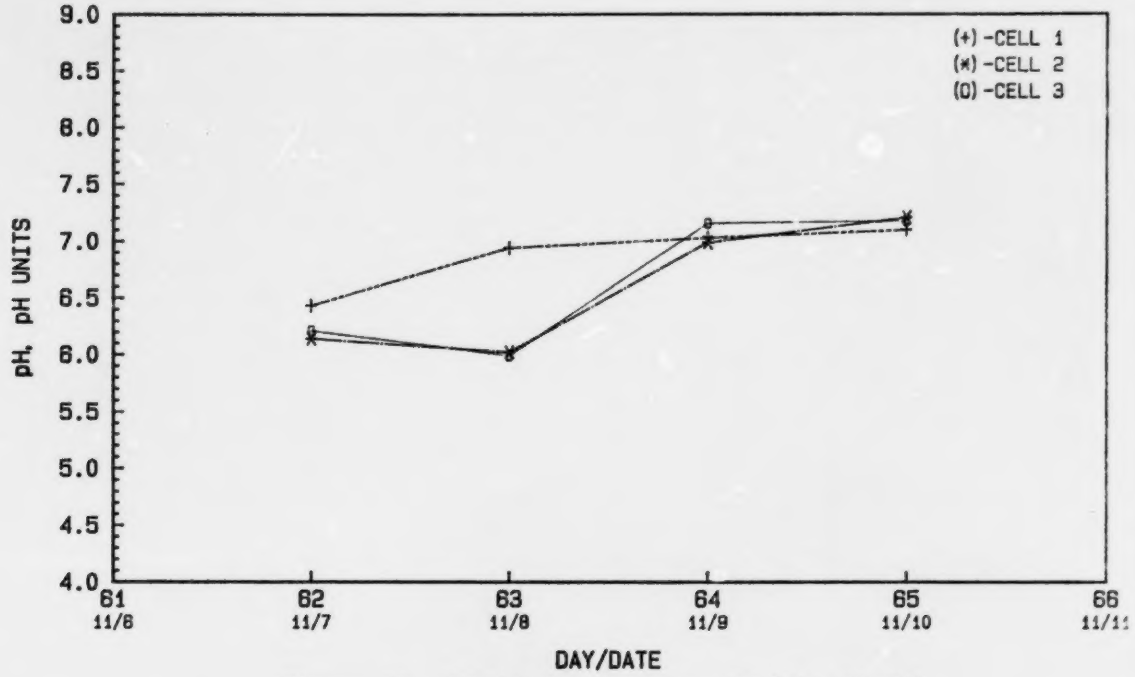


Figure 79. BTS-1 Mixed Liquor pH (Day 62-65).

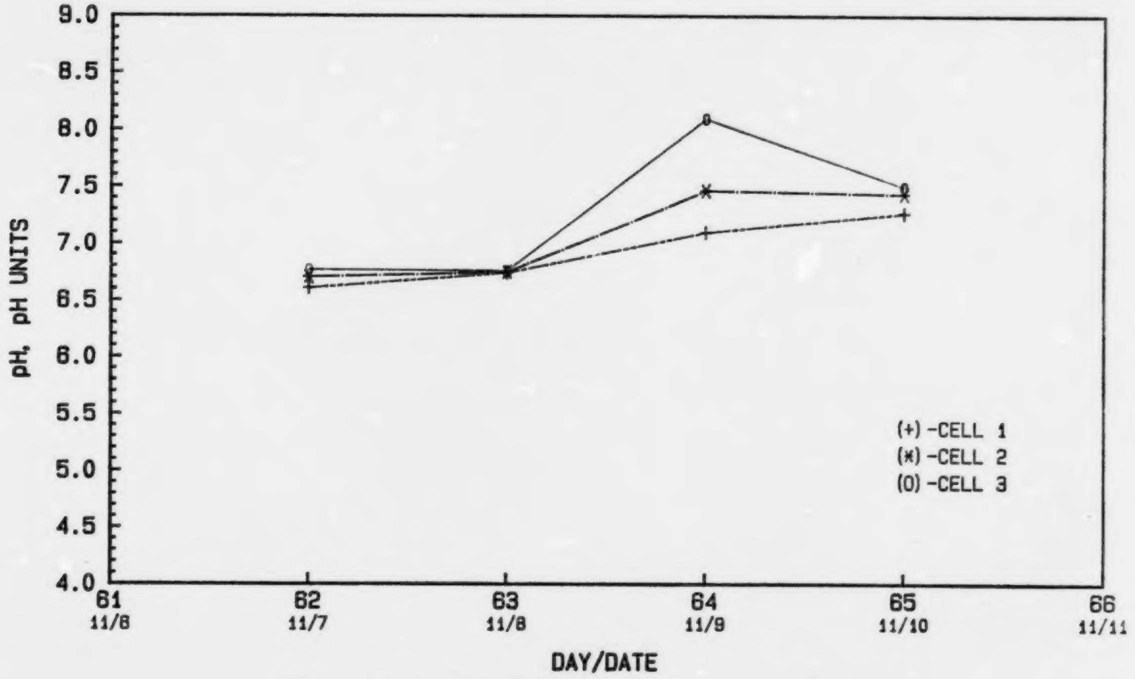


Figure 80. BTS-3 Mixed Liquor pH (Day 62-65).

2 mg/L during this period. The average mixed liquor suspended solids for BTS-3 (4770 mg/L) was very close to the 4790 mg/L average concentration measured during the first intensive period. The BTS-3 mixed liquor SVI was similar for the two test periods. The SVI for BTS-1 decreased with the increased PAC dosage. Mixed liquor settling rates remained very low. Effluent TCOD and SCOD values are shown on Figure 81.

BTS-2 Interim Test Period

A summary of the operation of the BTS-2 and BTS-3 pilot plants during the BTS 2 interim test period (Day 71-76, Nov 16-21, 1984) is presented in Table 26. Hydraulic and solids retention times were near the planned levels of 3 and 10 days, respectively. The temperature of BTS-2 mixed liquor was about 8°C lower than during the first intensive test period and averaged about 3°C lower than BTS-3 during this interim test period. Sodium hydroxide was added to control mixed liquor pH from Day 62 to 74 for BTS-2 and from Day 68 to 72 for BTS-3. The low BTS-3 mixed liquor pH occurred in each aeration tank cell on Day 71 during continuous addition of sodium hydroxide to cell 3. The aeration tank pH values for each unit are shown on Figures 82 and 83. With the exception of one low reading of 0.4 mg/L dissolved oxygen concentration in cell 1 of BTS-2 on Day 76, all other mixed liquor dissolved oxygen concentrations were 2 mg/L or greater for BTS-2 and BTS-3 during this test period. The average MLSS for BTS-3 was similar to the average levels in the first intensive test period. Mixed liquor

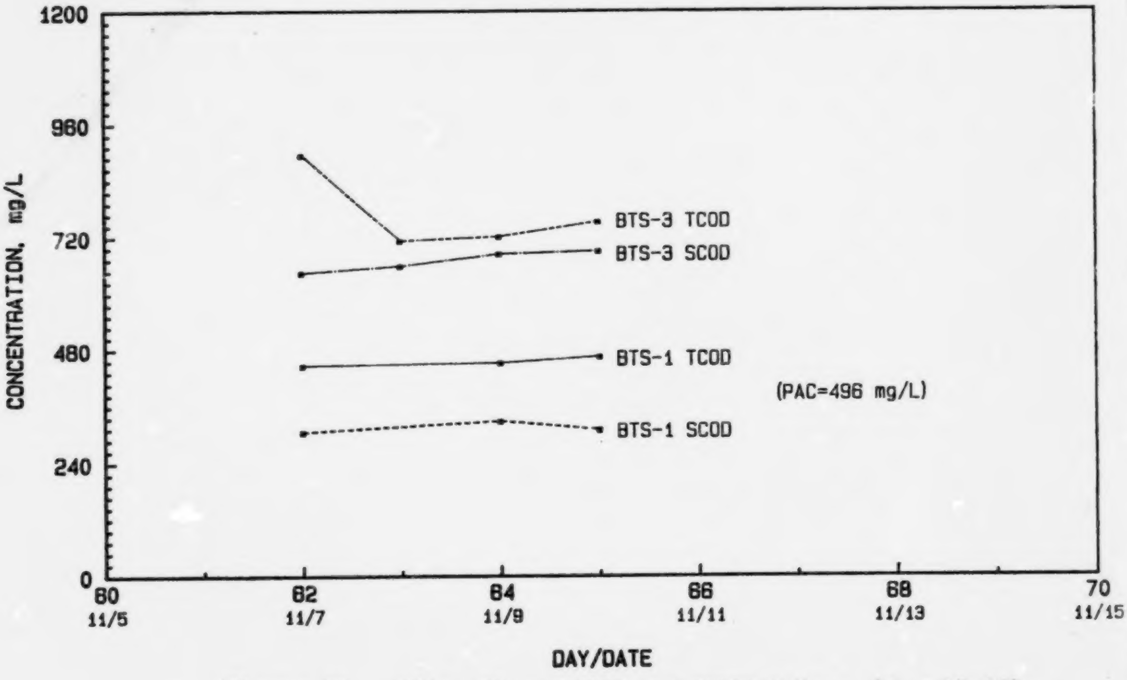


Figure 81. Pilot Plant TCOD and SCOD Values (Day 62-65).

TABLE 26. SUMMARY OF BIOLOGICAL PILOT PLANT OPERATION INTERIM TEST PERIOD FOR BTS-2 (DAY 71-76, NOV 16-21, 1984)

	BTS-2		BTS-3	
Parameter	Average (n)	Range	Average (n)	Range
Operation Data				
Feed Flow, L/min	1.27 (6)	1.24-1.29	0.044 (6)	0.041-0.045
PAC Flow, ml/min	32 (6)	31-32	*	
RS Flow, L/min	6.37 (6)	4.33-10.8	0.094 (6)	0.091-0.097
RS Flow, % of Feed	500 (6)	338-837	214 (6)	207-232
Waste ML Flow, ml/min	374 (6)	336-390	13 (6)	12-13
PAC Dosage, mg/L	1520 (6)	1500-1550	0	
F/M, g TCOD/day-g MLSS	**	**	0.79 (2)	0.65-0.92
HRT, days	3.0 (6)	3.0-3.1	3.0 (6)	3.0-3.2
SRT, days	10.0 (6)	9.5-10.9	9.8 (6)	9.3-10.0
Mixed Liquor Data				
Temp, °C	24 (18)	19-26.5	27 (18)	21-28
pH	***	6.7-7.5	***	6.1-7.4
DO, mg/L	3.4 (18)	0.4-6.4	4.9 (18)	3.5-6.4
TSS, mg/L	8830 (6)	8670-9280	4780 (6)	4480-4960
Effluent Data				
TCOD, mg/L	334 (5)	225-436	689 (6)	578-794
SCOD, mg/L	194 (5)	153-241	583 (6)	492-693
NIBOD, mg/L	12 (1)	-#	15 (1)	-#
NISBOD, mg/L	3 (1)	-#	4 (1)	-#
TSS, mg/L	108 (6)	41-220	96 (6)	63-145
VSS, mg/L	76 (2)	33-120	76 (2)	56-95

*PAC not added to BTS-3.
**F/M ratios not calculated for BTS-2 because of PAC in MLSS.
***Average pH values not calculated.
#Only one value.

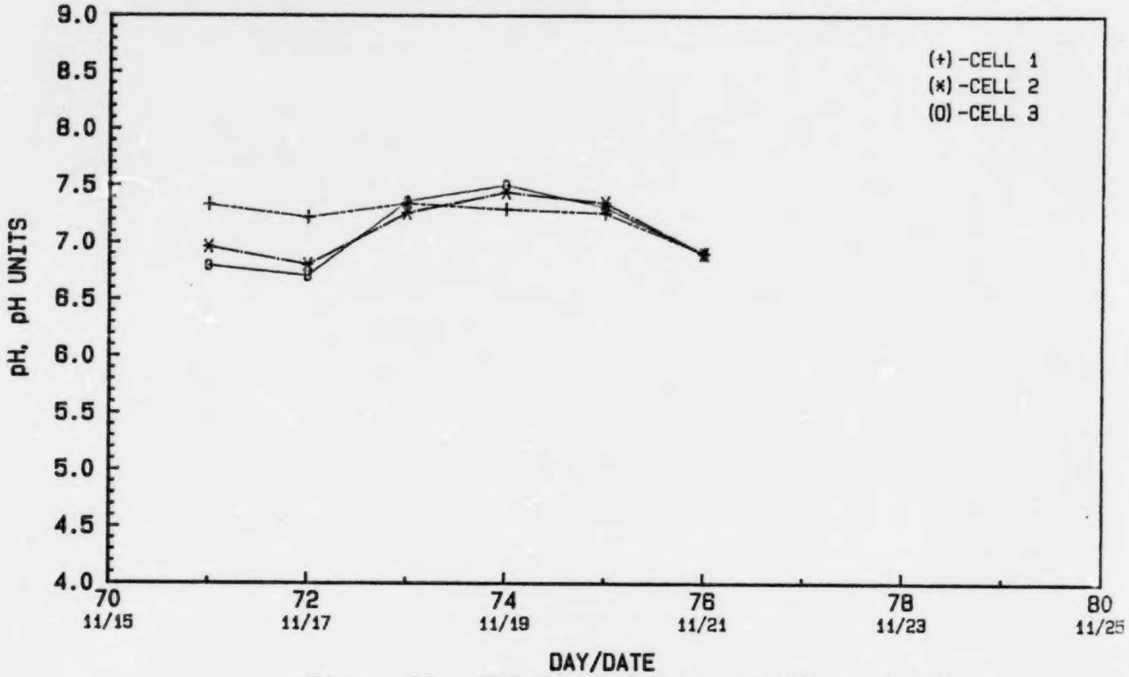


Figure 82. BTS-2 Mixed Liquor pH (Day 71-76).

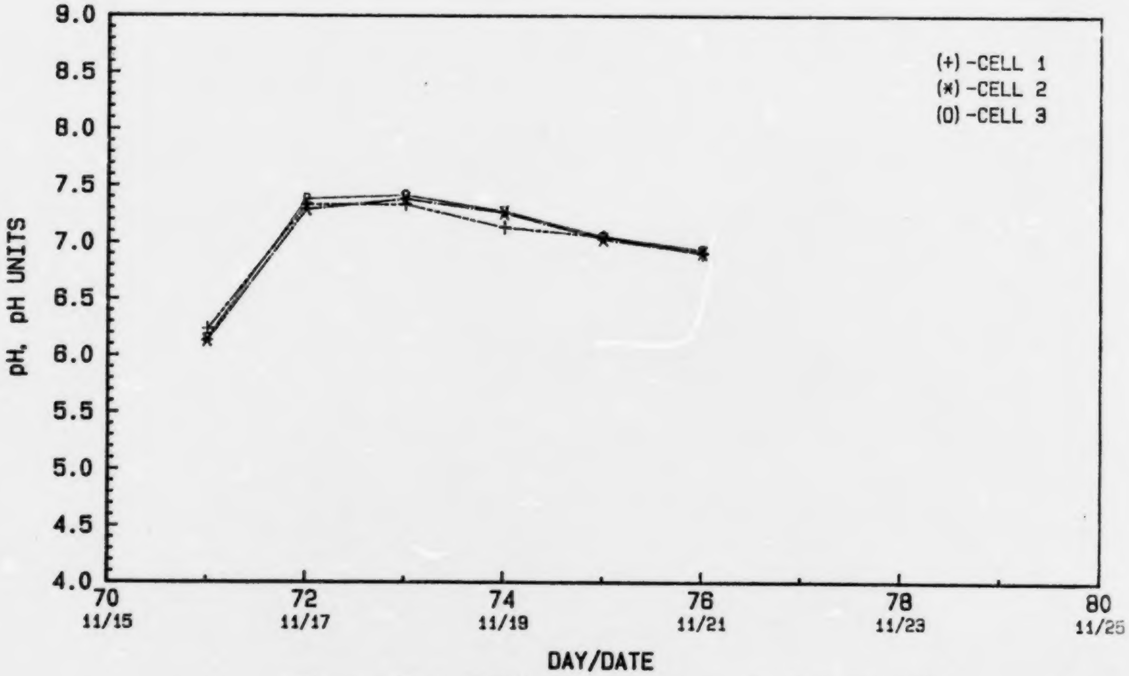


Figure 83. BTS-3 Mixed Liquor pH (Day 71-76).

settling tests were not performed during this interim test period so information concerning SVI and ML settling rate is not available. Effluent TCOD and SCOD values for BTS-2 and BTS-3 are shown on Figure 84.

SUMMARY

A comparison of average operating parameters and effluent quality for the tested PAC dosages during the intensive and interim test periods is presented in Table 27.

The addition of PAC resulted in some improvement in the sludge settleability, however, the mixed liquor solids settling rates remained at very low levels. The average settling rates for the three pilot plants during the first interim test period are shown on Figure 85 with the MLSS concentration. The average settling rate for the 496 mg/L PAC dosage was lower than the settling rate of the control during the same period (Days 62-65). It is believed, however, that the low settling rates measured for the 496 mg/L PAC dosage may have been an early indicator of the viscous floating solids that became apparent immediately after this test period.

The average mixed liquor oxygen uptake rate was similar for the pilot plant units being dosed with 208 and 827 mg/L PAC and the control unit. The units containing PAC had higher initial oxygen uptake rates (cell 1) than the control unit.

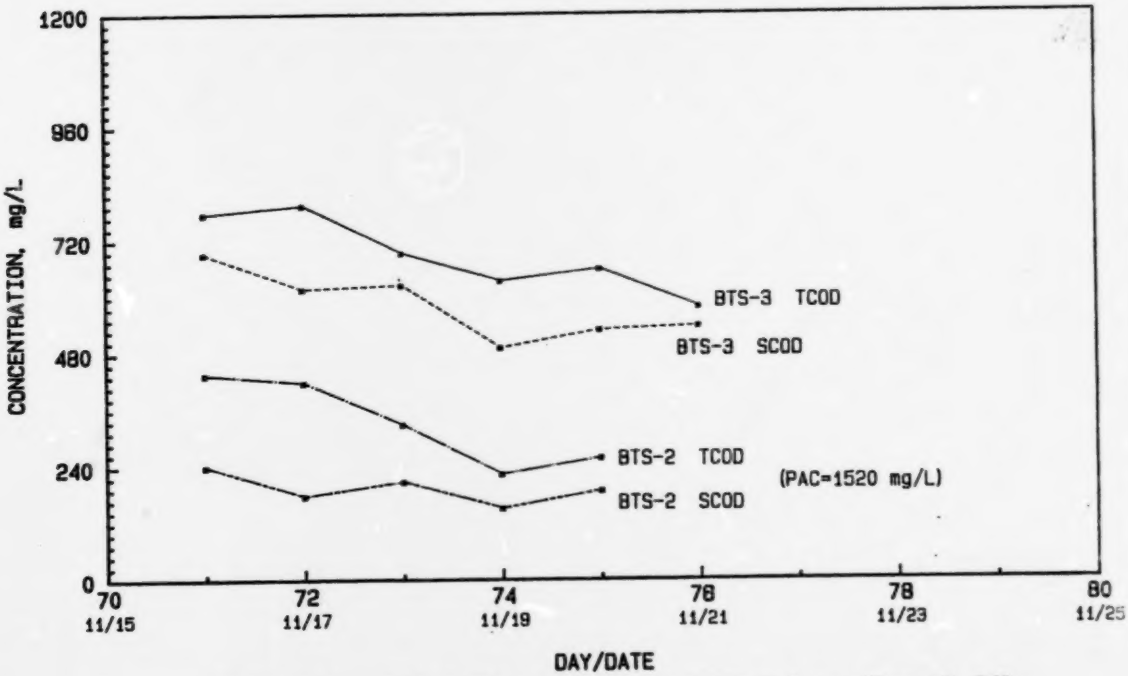


Figure 84. Pilot Plant TCOD and SCOD Values (Day 71-76).

TABLE 27. AVERAGE OPERATING PARAMETER AND EFFLUENT QUALITY VALUES FOR TESTED PAC DOSAGES

Tank PAC Dosage, mg/L Intensive Testing Period	BTS-3 0 Day 34-47	BTS-3 0 Day 62-65	BTS-3 0 Day 71-76	BTS-1 208 Day 34-47	BTS-1 496 Day 62-65	BTS-2 827 Day 34-47	BTS-2 1520 Day 71-76
Operational Data							
Feed Flow, L/min	0.044	0.045	0.044	1.34	1.38	1.26	1.27
PAC Flow, ml/min	*	*	*	18	31	18	32
RS Flow, L/min	0.163	0.092	0.094	3.01	3.80	4.08	6.37
RS Flow, % of Feed	370	204	214	225	275	324	500
Waste ML Flow, ml/min	13	13	13	420	419	367	374
PAC Dosage, mg/L	0	0	0	208	496	827	1520
F/M, g TCOD/day-g MLSS	0.64	0.69	0.79	**	**	**	**
Hydraulic Retention Time, days	3.0	3.0	3.0	3.1	3.0	3.1	3.0
Solids Retention Time, days	9.4	9.8	9.8	9.5	9.7	10.0	10.0
Mixed Liquor Data							
Temp, °C	31.5	28	27	32.5	27	32	24
pH (Range)	6.0-8.7	6.6-8.1	6.1-7.4	4.1-7.5	6.0-7.2	4.5-7.7	6.7-7.5
Dissolved Oxygen, mg/L	4.3	5.0	4.9	3.3	3.6	3.4	3.4
Suspended Solids, mg/L	4790	4770	4780	5850	7000	7690	8830
SVI, ml/g	204	206	***	171	142	130	***
Oxygen Uptake Rate, mg/L-min	0.95	***	***	0.83	***	0.83	***
Settling Rate, cm/min	0.007	0.036	***	0.032	0.015	0.045	***

(continued)

TABLE 27. (continued)

Tank PAC Dosage, mg/L Intensive Testing Period	BTS-3 0 Day 34-47	BTS-3 0 Day 61-65	BTS-3 0 Day 71-76	BTS-1 208 Day 34-47	BTS-1 496 Day 61-65	BTS-2 827 Day 34-47	BTS-2 1520 Day 71-76
Effluent Data							
TCOD, mg/L	1070	770	689	585	454	532	334
SCOD, mg/L	825	670	583	459	314	265	194
TOC, mg/L	290	***	***	158	115	110	***
NIBOD, mg/L	27	***	15	16	***	15	12
NISBOD, mg/L	<8	***	4	<6	***	<5	3
TSS, mg/L	143	44	96	85	59	190	108
VSS, mg/L	109	46	76	60	50	158	76
Removals							
Ave. Feed TCOD, mg/L	8120	7420	6810	8120	7420	8120	6810
TCOD Removal, %	86.8	89.6	89.9	92.8	93.9	93.4	95.1
SCOD Remaining, % of Feed TCOD	10.2	9.0	8.6	5.6	4.2	3.3	2.8

* PAC not added to BTS-3
** F/M ratios not calculated for BTS-1 and BTS-2 because of PAC in MLSS.
*** No measurements of this parameter during this test period.

Although minimization of suspended solids in the effluent was not an objective of these tests, a comparison of effluent suspended solids content can be made. The suspended solids in the effluent from the pilot plant receiving 208 mg/L PAC averaged 58 mg/L lower than the control unit suspended solids. At higher PAC dosages, however, the average PAC effluent suspended solids was 15, 47 and 12 mg/L higher than the average control TSS for PAC dosages of 496, 827 and 1520 mg/L, respectively.

The effect of added PAC on average effluent TCOD and SCOD is shown on Figure 86. The relatively large difference between TCOD and SCOD for the average PAC dosage of 827 mg/L is due to the average effluent suspended solids concentration which was substantially higher than for the other PAC dosages (see Table 27). Effluent SCOD is a better measure of unassimilated organic matter remaining after treatment. The SCOD curve on Figure 86 shows the reduction in SCOD with increasing PAC dosages.

The percent removal of TCOD is shown on Figure 87. Again, the relatively high suspended solids in the effluent from the run with an average 827 mg/L PAC dose affected the percent TCOD removal. The amount of SCOD remaining in the effluent, as a percentage of feed TCOD during the test period, is a better method of assessing the effect of PAC dosages on biological treatment. These data are shown on Figure 88. The effluent SCOD from the control unit ranged from 8.6 to 10.2 percent of the feed TCOD. The effluent SCOD from the PAC units ranged from 5.6 percent (208 mg/L PAC) to 2.8 percent (1520 mg/L PAC) of the feed TCOD.

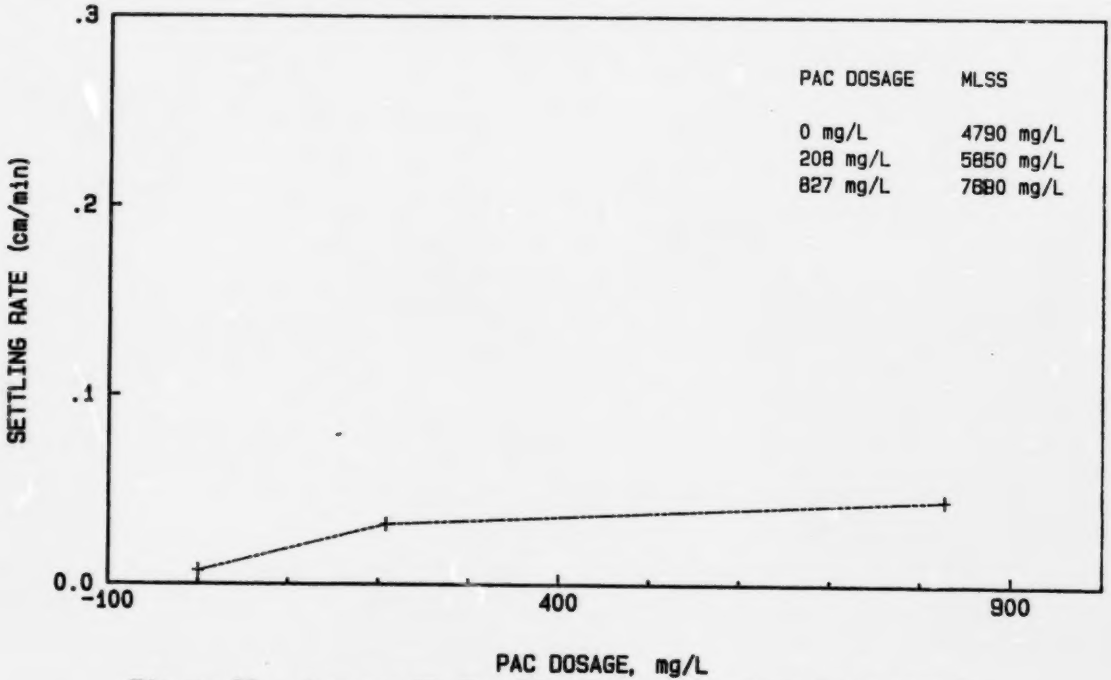


Figure 85. Average ML Settling Rate at Various PAC Dosages.

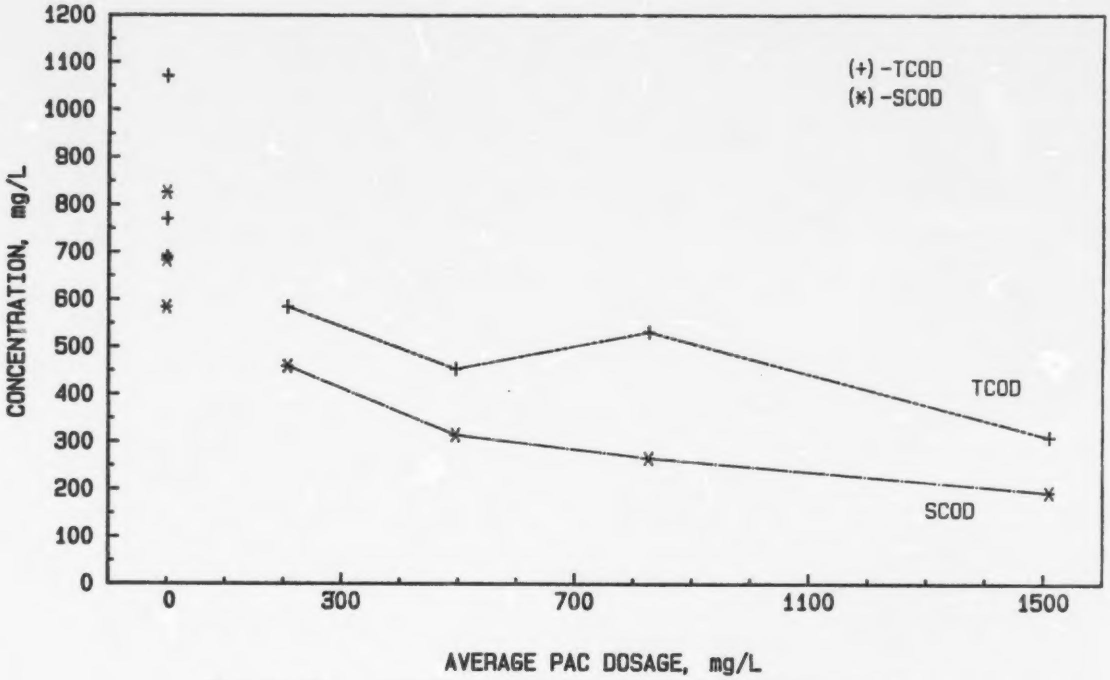


Figure 86. TCOD and SCOD at Various PAC Dosages.

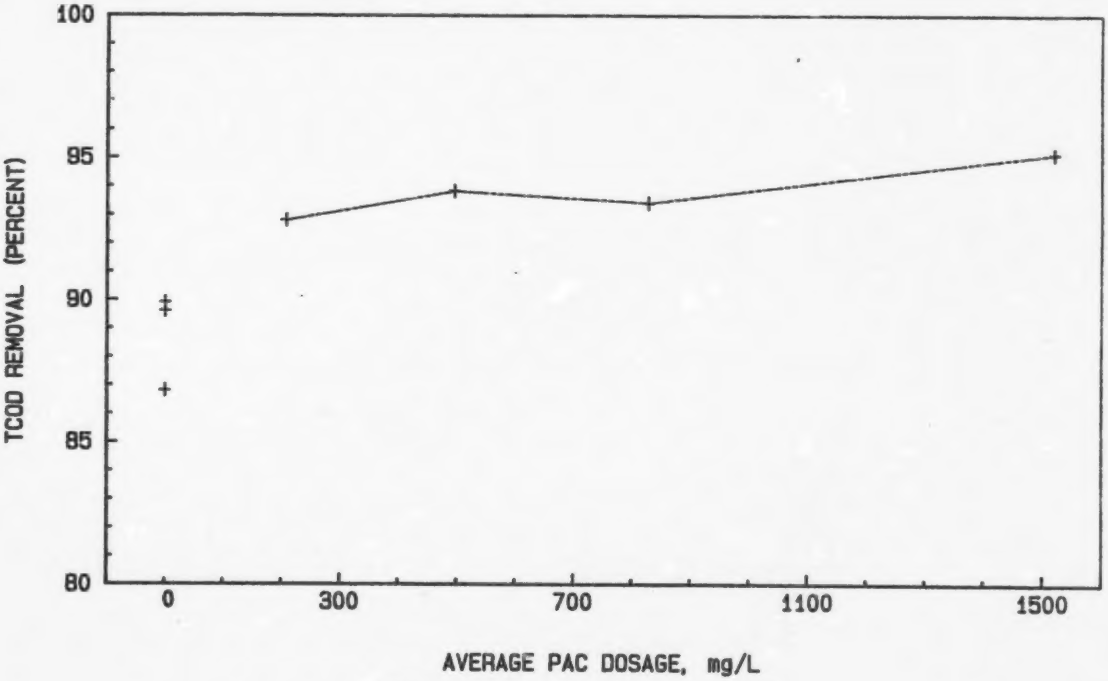


Figure 87. Removal at TCOD.

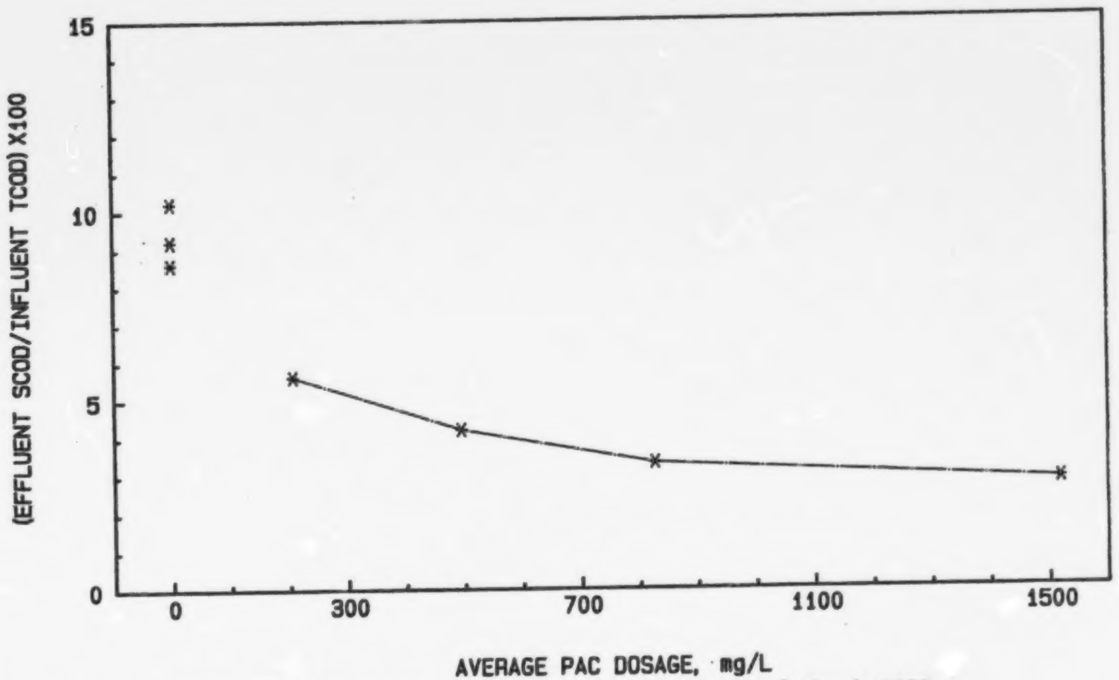


Figure 88. Effluent SCOD as a Percent of Feed TCOD.

SECTION 9

PHYSICAL-CHEMICAL PROJECT RESULTS

INTRODUCTION

This section presents a summary of the physical-chemical treatment findings at the pharmaceutical plant site. A discussion is presented for each of the technologies investigated (clarification, filtration and activated carbon). Information is also provided on the feedwater characteristics to the pilot plant during the pilot and bench testing studies.

The field study consisted of an extensive sampling and analytical program. Analytical results for all parameters tested are presented in Appendix A, Table A-1 and Appendix D. Pertinent highlights and selected data summaries are discussed in this section.

BENCH TESTING RESULTS

A series of laboratory bench treatment tests were performed on samples of the pharmaceutical plant effluent before and during the operation of the pilot plants. The objective of treatment was to investigate the pretreatment technologies (clarification and filtration) for suspended solids removal. The bench tests were performed to investigate various methods of chemical treatment, determine chemical types and dosages and indicate the effluent quality that might be expected from the pretreatment operations. The basic pretreatment process train tested for most of the study consisted of the addition of alum, rapid mix, addition of anionic polyelectrolyte, flocculation, sedimentation and filtration. Variations of this basic process that were studied using the pilot equipment included (1) clarification and filtration without chemical addition; (2) clarification with polymer followed by filtration; (3) clarification and direct filtration with polymer; and (4) clarification and direct filtration with alum and polymer. In addition, several chemical coagulants and coagulant aids were investigated either singularly or in combination. These included alum, ferric chloride, lime, bentonite clay, calcium chloride and several cationic and anionic polyelectrolytes. Caustic was also added as needed to maintain proper pH for chemical coagulation.

A grab sample for the first set of bench tests was collected from the full-scale plant secondary clarifier effluent on July 26, 1984. It was returned to the Rexnord laboratory in Milwaukee for testing. The results of these bench tests along with the chemical characteristics of the wastewater are summarized in Table 28.

The high suspended solids in the clarifier effluent indicated the need for pretreatment before carbon adsorption. Bench-top settling tests without chemical treatment produced an effluent with high suspended solids. Several organic polyelectrolytes were tested for effectiveness in flocculating the suspended solids: Percol 757, 763, 728, 721 and 455. Percol 757 (P757) was the most effective. Treatment with 5 mg/L P757 improved the settling rate from 0.3 cm/min (0.01 ft/min) with no polymer addition to 21.3 cm/min (0.7 ft/min). After a 30 minute settling time, the effluent resulting after polymer treatment had a suspended solids concentration of 29 mg/L. For comparison purposes, the sample settled without polymer had an effluent TSS of 114 mg/L. Based on these results, it was concluded that polymer in combination with clarification and filtration would provide adequate pretreatment of the wastewater. Inorganic coagulants such as alum or ferric chloride were not tried on this sample. The test plan was designed based upon these results.

The pilot equipment arrived at the plant site about one month (8/31/84) after the initial bench tests were performed. A second series of treatability tests were performed from 9/5 to 9/8 using the plant secondary clarifier effluent and varying concentrations of polymer. The test results, summarized in Appendix D, Tables D-1 to D-3, concluded that polymers alone at dosages up to 30 mg/L were not effective in producing an effluent with low TSS. On 9/10 a local source of alum was found and another series of

TABLE 28. RESULTS OF 7/26/84 BENCH SCALE TREATMENT TESTS

Parameter	Value	
SBOD, mg/L	108	
SCOD, mg/L	1310	
pH, units	7.9	
TSS, mg/L	270	
VSS, mg/L	250	
Settling Test Data		
Test No.	1	2
Polymer Type*	-	P757
Polymer Dosage, mg/L	0	5
Flocculation Time, min.	0	2
Settling Rate, cm/min	0.3	21.3
Settling Time, min	30	10
Sludge Volume, L/1000 liters	40	55
Effluent TSS**, mg/L	114	29

* Several polymers were screened.
P757 provided the best floc based on visual observation.

** Unfiltered.

tests were performed (Appendix D, Table D-4). Bench testing indicated that a dosage of 200 mg/L alum plus 2 mg/L polymer (P757 - a high molecular weight cationic polyelectrolyte) treated the clarifier effluent to low TSS levels. On 9/13 samples of the clarifier effluent were sent to the Rexnord laboratory for testing. Several coagulants were studied including alum, ferric chloride, lime, calcium chloride, and bentonite clay. Polymers were rescreened and an optimum selected (P728). The P728 is a medium charge, very high molecular weight cationic polymer. The treatment results are summarized in Appendix D, Tables D-5 and D-6. After evaluating several combinations of coagulants and coagulant aids, it was concluded that the best treatment was achieved by using about 400 mg/L alum and 2 to 4 mg/L P728 polymer. Addition of alum in excess of 400 mg/L reduced the pH to less than 6.5 which caused the floc to float. Similar results were observed in the field. Bench tests were conducted routinely on-site for the remainder of September, 1984 (Appendix D, Table D-7). In general, it was found that increasing dosages of alum were required to achieve an effluent low in TSS. Switching the feed source to the pilot system from the secondary clarifier effluent to the plant final effluent on 9/17 did not decrease chemical requirements. Also, the plant effluent alkalinity appeared to be variable. On some days, the selected alum dosage would cause the feedwater pH to drop to 6.2 to 6.5 resulting in floating floc. On other days, this was not observed.

Polymer screening and chemical dosage tests continued throughout the study. On 10/5, an ultra-high molecular weight, anionic polyelectrolyte, P727 was found to produce a faster settling floc than the P757 that was in use in the pilot system. Prior to this time it was found that some polymers would work very good on one day but not at all on the next day. The change was very rapid and this created problems in operation of the pilot equipment. Suspended solids would increase in carryover from the clarifier to the filter and carbon columns resulting in high headloss and automatic shutdown of the filter and activated carbon systems. This also increased the backwash frequency.

By mid-October, alum dosages as high as 1500 mg/L were being evaluated (Appendix D, Tables D-8 to D-13). Polymer dosage tests concentrated on minimizing the amount of polymer being added. Experience with the pilot clarifier had determined that excess polymer tended to produce TSS that settled well but formed a bridge in the bottom of the clarifier cone, making removal of the sludge very difficult. Normal maintenance practice would include mechanical scraping of the settled solids from the clarifier cone bottom, however, the pilot clarifier was not fitted with a sludge scraper mechanism. This design deficiency contributed to the problem to the extent that occasionally some of the unremoved sludge would turn septic and float to the surface. By carefully controlling polymer dosage, this effect was minimized.

The bench tests conducted in November (Tables D-14 to D-17, Appendix D) were used primarily for process control. Alum dosages studied ranged from 800-1500 mg/L and polymer dosage (P727) was varied from 0.4 to 1.0 mg/L.

One bench test was performed to determine if polymer could improve the filterability of clarified effluent. On October 21 (Appendix D Table D-18), various dosages of P727 and P728 were added to samples of the pilot scale clarifier effluent. After mixing for 15 seconds the samples were filtered through Whatman 541 paper to approximate filtration. Effluent turbidities were measured and compared. The study determined that polymer provided a slight improvement in effluent quality and should be considered in the pilot filtration system. Beginning October 23 polymer addition at 1 mg/L was studied as a filtration aid.

FEED WASTEWATER CHARACTERISTICS

Twenty-four hour composite samples of the pharmaceutical plant effluent were collected throughout the study. At the start of the physical-chemical pilot testing (9/8 to 9/16), the pilot feedwater source was the full-scale plant secondary clarifier effluent. From 9/17 to the end of the study (12/4), the plant final effluent served as the source of feedwater to the pilot system. (See Figure 1).

Table 29 presents a summary of the feed wastewater characteristics during the study. Separate columns are provided for the testing periods when secondary clarifier effluent and final plant effluent were used as pilot system feedwater sources. The last two columns of Table 29 present the combined study period results. In reviewing the secondary clarifier effluent data summary, it is evident that suspended solids were quite variable, ranging from 72 mg/L to 1560 mg/L for 9 days of testing. This extreme TSS variation was the main reason for relocating the intake to the plant final clarifier beginning on 9/17. For comparison, the full-scale plant effluent suspended solids ranged from 65-600 mg/L for 71 samples and averaged 280 mg/L. TCOD values typically increased with increases in suspended solids. This is particularly evident by reviewing Figure 89. The principal parameters of concern (TCOD, SCOD, TSS, TBOD) for this study are presented on a plot of concentration versus days of operation.

For the entire testing period, the TBOD averaged 151 mg/L for the 33 analyses performed. The TCOD average was 1410 mg/L while the average SCOD in the feedwater was 830 mg/L (59% of the TCOD). The SCOD concentration range varied from 412 - 1330 mg/L. The wastewater pH was relatively constant over the study period, ranging from 7.7 to 8.6 pH units.

All of the daily analytical values for the feed wastewater to the pilot system are in Table D-19, Appendix D.

CLARIFICATION RESULTS

The primary purpose of clarification was to remove suspended solids present in the pharmaceutical plant effluent. The pilot scale clarifier was operated continuously throughout the testing program.

TABLE 29. FEED WASTEWATER COMPOSITE SAMPLE ANALYSIS SUMMARY (SAMPLE POINT J)

	Secondary Clarifier Effluent 9/8 - 9/16/84		Final Plant Effluent 9/17 - 12/4/84		Total Study	
Parameter	Average (n)	Range (n)	Average (n)	Range (n)	Average (n)	Range (n)
TBOD, mg/L	117 (2)	74-160	153 (31)	61-360	151 (33)	61-360
TSS, mg/L	775 (10)	72-1560	280 (71)	65-600	341 (81)	65-1560
TCOD, mg/L	1815 (10)	776-3180	1319 (47)	730-2580	1410 (57)	730-3180
SCOD, mg/L	*	*	830 (55)	412-1330	830 (55)	412-1330
pH, units		7.7-7.8(9)		7.7-8.6(71)		7.7-8.6 (80)
Temperature, °C	37 (7)	34-40	22 (50)	14-30	24 (57)	14-40

*No data taken.

The feed rate to the pilot clarifier was 17-23 L/min (4.5 - 6.0 gpm). Early in the study, various flocculation speeds were evaluated. A speed of 9 revolutions per minute was found to be acceptable for enhancing flocculation with minimal shearing effect. As mentioned previously in the bench scale testing discussion, several combinations of chemicals were evaluated to investigate suspended solids removal. A coagulant combination that consistently produced a good quality effluent was not found during this study.

Initially (9/5 - 9/8), the full-scale plant secondary clarifier effluent was run through the pilot clarifier with no chemical addition. However, effluent quality was quite poor. By 9/10, bench tests had determined that a combination of alum and polyelectrolyte warranted study and their use was initiated. An initial alum dosage of 200 mg/L was selected based upon the bench test results along with 2 mg/L of polyelectrolyte (P757). By 9/21 the alum dosage had been increased to 495 mg/L. Between 9/21 - 10/16, the alum dosage was varied from 495 mg/L to 670 mg/L depending on bench test results. During this period, effluent quality remained poor. In some cases, suspended solids in the effluent exceeded that in the influent. Often, a chemical dosage that worked one day did not work the next. Similarly, polymers had to be varied to insure good floc formation. On 10/5, P727 polymer was substituted for P757.

On 10/18, alum concentration in the feed stream was increased to 792

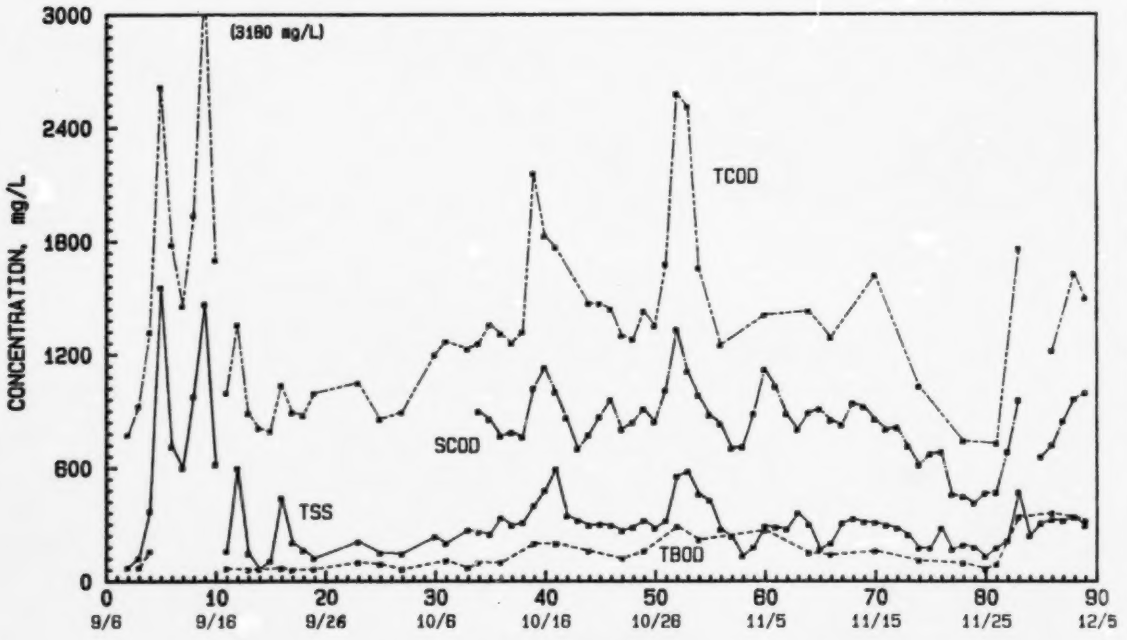


Figure 89. TCOD, SCOD, TSS and TBOD Concentration Versus Days of Operation.

mg/L. This was further increased to a maximum of 1340 mg/L on 10/20. It is possible that a portion of the alum that was being added was actually tied up with excess phosphate in the influent. Thus, all of the alum would not have been available for coagulation. During this same time period, polymer dosages were decreased to between 0.2 - 0.4 mg/L. The sludge being produced from the system was very difficult to pump from the clarifier bottom. The sludge would tend to set up along the walls of the clarifier cone and turn septic. The sludge would then float to the surface and increase the suspended solids in the effluent. Reducing the amount of polymer added to the feedwater improved the pumpability of the sludge and minimized the amount of material being carried over to the filter.

Sludge was wasted on a continuous basis throughout the study. Bench settling tests provided an estimate of the amount of sludge produced per liter of water treated. The sludge pump was set at a corresponding wasting rate. Sludge wastage was fine tuned by measuring the sludge blanket in the clarifier using the taps provided along the clarifier wall. Due to the natural tendency of the sludge to float, the sludge blanket was kept at a minimum.

Difficulty in settling the TSS in the influent water was also experienced, especially during periods of high alum dosage. As alum dosage was increased, the pH of the water to be clarified would decrease. When the pH dropped below 6.5 the floc would float. To minimize this effect, caustic soda was added to the influent stream at the mix tank where the alum was added. Typical concentrations of sodium hydroxide required to adjust the pH in the clarifier influent to 6.5 are shown in Table 30. Dosages of the sodium hydroxide required ranged from zero when no alum was added to as high as 306 mg/L for an alum dosage of 1200 mg/L. Some brief on-site flotation tests were also performed on the influent wastewater. Dissolved air flotation would be a good candidate technology because of the natural tendency of the sludge to float. In the few tests that were performed with alum and polymer a very clear subnatant was produced. The rise rate was also excellent (> 30.5 cm/min). No further testing was performed since a dissolved air flotation unit was not available for this study.

TABLE 30. SODIUM HYDROXIDE TYPICALLY REQUIRED TO MAINTAIN A MINIMUM FEEDWATER pH OF 6.5

Alum Dosage, mg/L	NaOH Dosage to pH 6.5, mg/L
0	0
500	35
800	154
1000	202
1200	306

The chemical clarification operating performance data summary is presented in Appendix D, Table D-20.

The analytical data summary for the clarifier effluent composite samples (sample point "K") collected during the study is shown in Table D-21, Appendix D. A summary of the clarifier efficiency is shown in Table 31. In reviewing Table 31, it can be seen that clarification reduced the influent concentration of suspended solids by 43 percent. During the study, the average clarifier effluent suspended solids was 171 mg/L. At selected periods during the study, TSS removals as high as 89 percent were achieved. Daily clarifier influent and effluent TSS concentration are plotted on Figure 90. All of the data points available for both influent and effluent during the entire study have been plotted. Note that on occasion, the effluent suspended solids were higher than the influent concentration. This was caused by floating sludge that carried over the weir. The clarifier effluent TBOD averaged 89 mg/L. This represented a 44 percent removal. TBOD data for influent and effluent are presented graphically on Figure 91. TCOD was another parameter of performance that was evaluated during the study. For the 43 TCOD data sets the influent TCOD averaged 1360 mg/L compared to 977 mg/L for the effluent. This is equivalent to a 28 percent removal across the pilot scale clarifier. Figure 92 illustrates the influent and effluent TCOD values for the clarification process. SCOD was reduced by 17 percent across the clarifier based on 51 observations. The pH of the feedwater remained quite stable during the test period, ranging from 7.7 to 8.6.

In comparison, the effluent pH range varied from 6.4 to 7.9. This slightly lower effluent pH range was caused by the alum addition. Temperature of the clarifier influent and effluent decreased consistently with the onset of colder weather. At the start of the study, the influent temperature was at 34°C and by early December, temperature readings for both

TABLE 31. CLARIFICATION EFFICIENCY*

Parameter	Influent (n)**	Effluent (n)**	% Removal (n)
TSS, mg/L	301	171	43 (65)
TBOD, mg/L	158	89	44 (29)
TCOD, mg/L	1360	977	28 (43)
SCOD, mg/L	828	689	17 (51)
pH, units	7.7-8.6 (67)	6.4-7.9 (67)	
Temperature, °C	14-37 (42)	15-36 (42)	

* The influent/effluent comparison was made only when both values were available.

** Average values for TSS, TBOD, TCOD, SCOD. Range for pH and temperature.

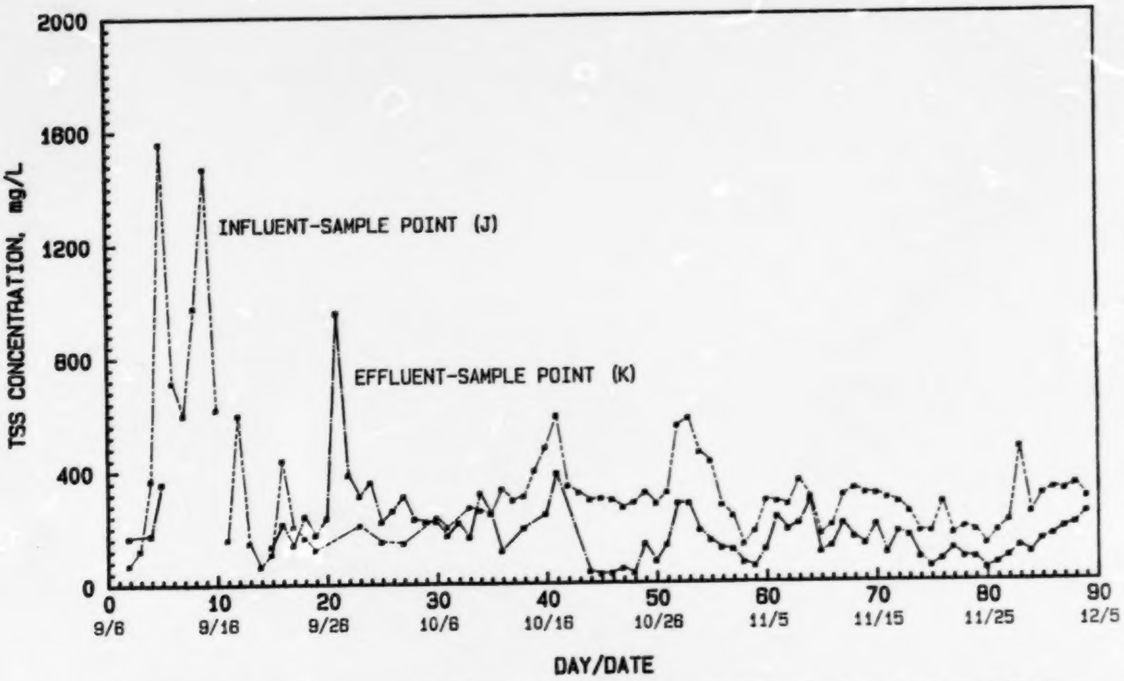


Figure 90. Clarifier Influent and Effluent TSS Concentration Versus Days of Operation.

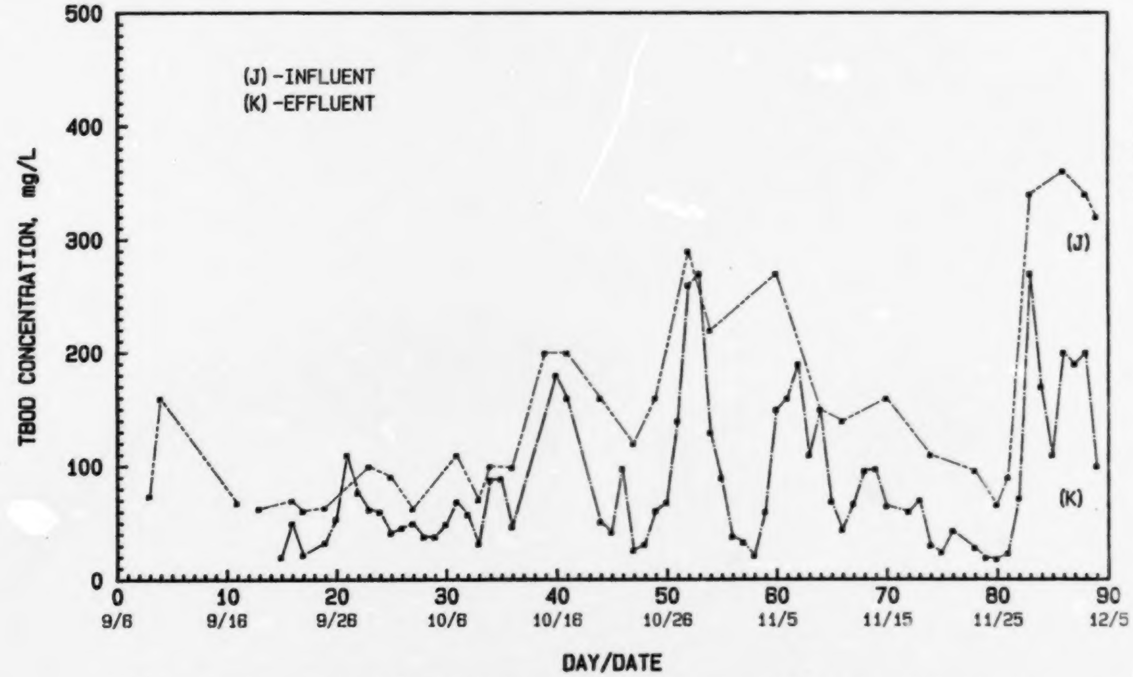


Figure 91. Clarifier Influent and Effluent TBOD Concentration Versus Days of Operation.

the clarifier influent and effluent were typically about 15°C.

Gravity Settling Tests

Batch gravity settling tests were performed periodically during the study. The test procedure involved filling a graduated cylinder to the 1000 ml level and recording the volume of the solids/liquid interface versus time. The settling test samples were taken from a sample tap located just prior to entering into the pilot clarifier center well. At this location, alum had been added to the wastewater, but not polymer. Polymer was added to the cylinder at the same dosage as that being added to the clarifier at the time the sample was withdrawn. The sample was then flocculated for about 1 minute to simulate the clarifier flocculation zone. Following flocculation, the sample was allowed to settle and the interface was recorded at regular intervals.

From the information obtained in the settling tests, it was possible to construct settling rate curves (first 30 minutes) for several operating days. The settling test data are summarized in Appendix D, Tables D-22 to D-27 and on Figures D-1 to D-12. On 10/13 seven settling tests were performed to evaluate chemical dosage versus rate of settling. For these runs, alum dose was varied from 0 to 788 mg/L. Similarly, polymer (P727) concentration ranged from 0 to 3.3 mg/L. The best settling rate (30.5 cm/min) was achieved for Run No. 1 at a dosage of 495 mg/L alum plus 3.3

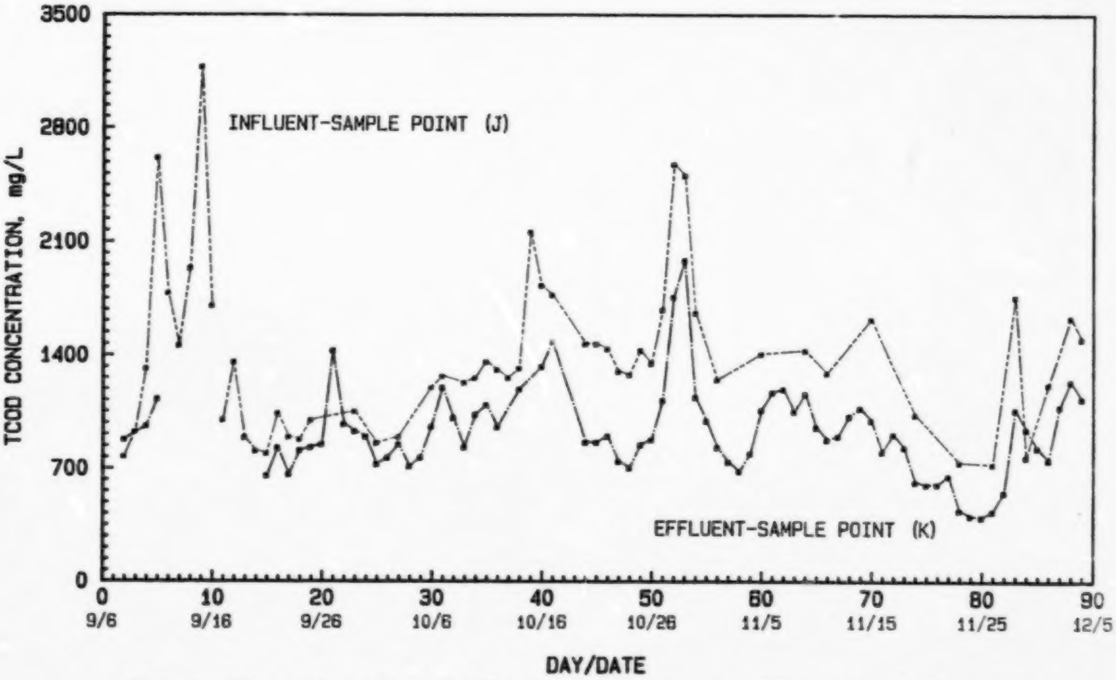


Figure 92. Clarifier Influent and Effluent TCOD Concentrations.

mg/L P727 polymer. The poorest settling rate was observed for Run No. 7 in which no chemical was added. The settling rate for this test was 3.9 cm/min. In reviewing the data, the settling rate appeared to be independent of alum dosage but closely related to the amount of polymer added. In general, settling rate improved with increased concentration of polymer. However, polymer dosages in excess of 1 mg/L were typically not added to the clarifier feedwater because of the tendency of the settled sludge to bridge as discussed previously.

In two settling tests performed on 10/21 alum dosages of 1240 and 1250 mg/L were added. The polymer dosage (P727) was held constant for each test at 0.37 mg/L. Settling rates of 3.8 cm/min and 2.2 cm/min were achieved, respectively.

Another settling test was performed on 10/25. Alum and P727 polymer concentration of 975 mg/L and 0.37 mg/L were added, respectively. The corresponding settling rate was 3.0 cm/min. On 11/30, two duplicate settling tests were conducted at an alum dosage of 1240 mg/L and a polymer (P727) dosage of 0.44 mg/L. These tests had settling rates of 5.8 cm/min and 7.8 cm/min.

Gravity Thickening Tests

Two gravity thickening tests were performed on a clarifier sludge sample collected during a period when the system was operating at steady state condition (10/21). The sludge thickening test data are summarized in Appendix D, Table D-28 and on Figures D-13 and D-14.

In test No. 1, the sludge was allowed to settle for 85 minutes. Position of interface (POI), cm versus time in minutes was determined. The thickening rate was determined to be 0.03 cm/min. The second sludge thickening test was run for 120 minutes and the thickening rate was 0.09 cm/min.

Conducting in-depth gravity thickening tests (preparation of various dilutions and construction of flux concentration curves) was outside of the scope of this project.

MULTI-MEDIA FILTRATION

Multi-media filtration was used as a polishing step following clarification of the pharmaceutical plant effluent. The filtration testing was performed over the entire duration of the study (September - December, 1984).

The multi-media filtration effluent composite sample analytical data collected during the project are summarized in Appendix D, Table D-29. This table presents all of the analyses performed for sample point "L". A summary of the removal efficiency across the filter is presented in Table 32. Influent and effluent samples were collected over 24 hour periods. The multi-media filter effluent was not sampled during backwash events.

Multiple filter runs were normally performed each day. For the seventy days for which influent and effluent composite sample values were available, suspended solids removal averaged 26 percent. The average effluent TSS concentration was 121 mg/L. The data in Table 32 also illustrate that TBOD and TCOD removals were very poor averaging 2 and 3 percent, respectively.

In an effort to improve solids capture, polymer (P727) was added at a concentration of 1 mg/L from 10/24 to 11/04. The polymer was added to the inlet side of the multi-media filter feed pump. Suspended solids removal during this period actually decreased to 22 percent. Reviewing Table 33 it can be seen that average TBOD and TCOD removal also decreased slightly. Beginning on 11/5, 10 mg/L of alum plus 1 mg/L of P727 polymer was added to the filter feed. The alum was added in the holding tank providing the feed source to the filter. The polymer was added in-line downstream of the alum addition point. The alum plus polymer addition continued until 11/20.

Referring to Table 33, it is evident that no improvement in effluent quality was achieved as measured by TSS, TBOD and TCOD.

Throughout the pilot program, the same backwash procedure was used as discussed previously in Section 5. There was no observable deterioration of filter effectiveness as measured by the initial headloss or other performance parameters using a wash rate of 6110 L/m^2-backwash (150 gal/ft^2 backwash). There was, however, a significant loss of filter media observed during the study. At the completion of the pilot tests, the filter media depth was checked. The total amount of media left in the filter was 79 cm (31 inches). This compares to an initial depth of 119 cm (47 inches). On disassembly of the filter it was evident that the majority of the loss

TABLE 32. MULTI-MEDIA FILTER REMOVAL EFFICIENCY* (9/8-12/4)

Parameter	Influent(n)**	Effluent(n)**	% Removal(n)
TSS, mg/L	163	121	26 (70)
TBOD, mg/L	83	81	2 (65)
TCOD, mg/L	907	877	3 (70)
SCOD, mg/L	653	657	0 (69)
pH, units	6.4-7.9 (72)	6.4-8.1 (72)	
Temperature, °C	15-36 (24)	17-35.5 (24)	

*The influent/effluent comparison was made only when both values were available. Effluent data are not typical of a well designed and operated filter and are presented only for informational purposes.

**Average values for TSS, TBOD, TCOD and SCOD. Range for pH and temperature.

occurred from anthracite coal washout. While removing the remaining media, it was observed that the coarse garnet sand was at the bottom of the filter. Fine garnet sand was found mixed with the silica sand and some coal was found in the silica sand near the surface of the media. No mudballs were found in the media.

It was evident from the data and the post-test observation of the filter media that the filter did not perform as expected. Problems with the backwash system apparently did not allow the multi-media filter bed to stratify following the backwash cycle. It is possible that the failure of the bed to stratify was due to a flaw in the design of the filter, as discussed previously in Section 5. The plots on Figure 93 further reinforce this theory. Shown is a graph of an actual (11/8/84) clean water headloss curve using data collected from the filter immediately after backwash. A second curve plots the theoretical headloss. Notice that the 11/8/84 curve does not show any of the distinct breaks that can be seen on the theoretical curve. This suggests media intermixing caused by inadequate backwash capability.

Although other filtration data were collected, they were considered unreliable and not representative of multi-media filtration. Detailed evaluation would be of very little value and was not performed.

TABLE 33. COMPARISON OF FILTER PERFORMANCE FOR SELECTED PERIODS*

Type of Chemical Addition	9/8-10/23	10/24-11/4	11/5-11/20	11/21-12/4
	None	1 mg/L P727	10 mg/L Alum 1 mg/L P727	1 mg/L P727
TSS**				
INF, mg/L	199	136	157	121
EFF, mg/L	133	106	134	92
% REM	33 (28)	22 (12)	15 (16)	24 (14)
TBOD**				
INF, mg/L	56	100	86	111
EFF, mg/L	51	102	86	110
% REM	9 (26)	- (12)	0 (15)	1 (13)
TCOD**				
INF, mg/L	908	1040	929	752
EFF, mg/L	860	1020	871	736
% REM	5 (29)	2 (12)	6 (16)	2 (14)

*Effluent data are not representative of a well designed and operated filter and are presented only for informational purposes.

**Average concentration.

( ) Indicates number of data points used to obtain average.

GRANULAR ACTIVATED CARBON RESULTS

Granular activated carbon (GAC) was evaluated on a pilot scale to determine its ability to remove soluble organics from the pharmaceutical plant effluent. Two runs were conducted using four columns in series. Run No. 1 was performed from 9/11 to 10/12 with operation of the four columns in the downflow mode. Run No. 2 was from 10/24 to 12/04 and was performed using the upflow mode of operation. The wastewater that was treated during both runs by the activated carbon consisted of pharmaceutical plant secondary effluent that had been pretreated by the pilot chemical clarification and multi-media filtration systems discussed previously.

An integral part of the activated carbon pilot study was the extensive sampling program conducted and resulting analytical data generated. This sampling program consisted of the collection of daily 24 hour composite samples from the GAC influent and effluent for both runs. Analysis on these samples included TSS, TBOD, TCOD and SCOD.

As shown previously in Table 7 as part of the Section 6 Pilot Project Test Plan writeup, grab samples were collected once per day from nine locations around the activated carbon columns during GAC Run No. 1. These included the influent and effluent from each column as well as each column midpoint. The samples were analyzed for SCOD. For GAC Run No. 2, all

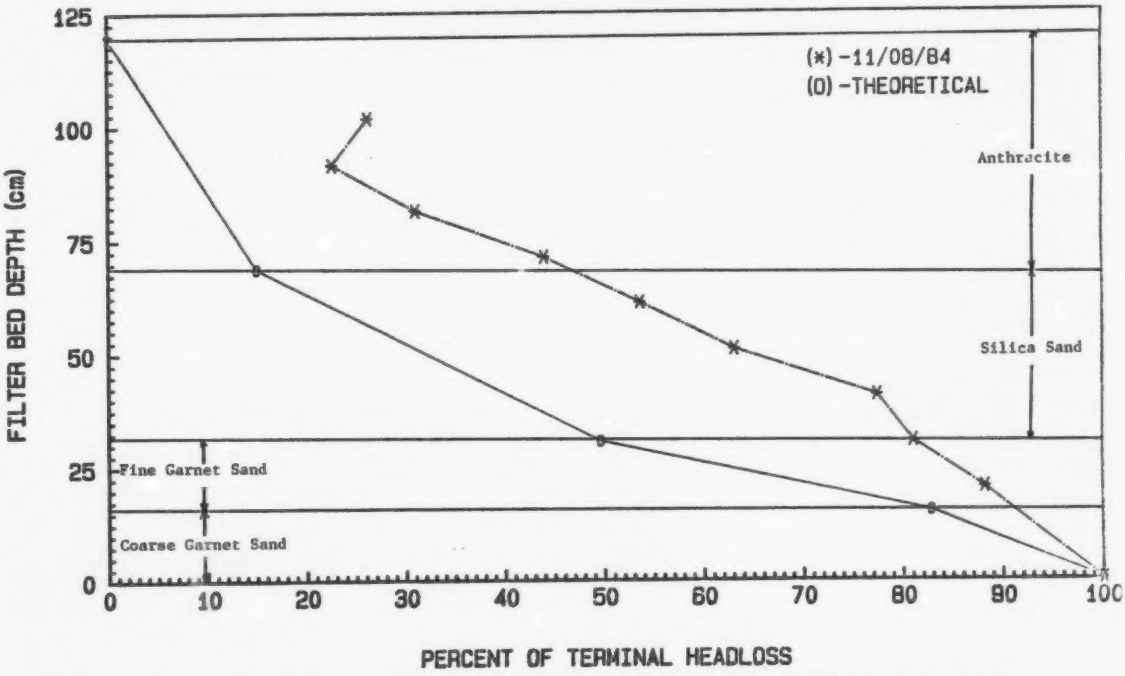


Figure 93. Clean Filter Bed Headloss Profile Curves.

midpoint column samples were eliminated because of the shorter beds in each column in the upflow operation. Thus, only the influent and each of the four column effluents were sampled (grabs) and analyzed for SCOD.

A summary of the GAC composite and grab sample analyses for the two runs is presented in Appendix D, Tables D-30 and D-31.

Since TBOD was analyzed from sample point L and not M, Table D-32, shown in Appendix D, has been prepared to evaluate TBOD removal across the carbon column system. In this table, TBOD values for sample points L and N are compared.

GAC Run No. 1 Grab Sample Results

During the 18 days of testing for GAC Run No. 1, 149,959 liters (39,091 gallons) of pretreated pharmaceutical plant effluent was pumped through the activated carbon columns. The daily volume of wastewater pumped through the columns between sets of grab samples is shown in Table 34. The average flow rate through the carbon system during the first test run was 6.1 L/min (1.6 gpm). This was equivalent to an empty bed contact time of 26 minutes per column or 104 minutes in total for the four columns.

Table 34 also presents the results of the grab sample SCOD analysis for each day of testing during Run No. 1. The times and cumulative volume processed for each date in Table 34 corresponds directly to the sampling intervals. SCOD was the only parameter measured on the grab samples. The test data shown in Table 34 were used to evaluate the efficiency of the activated carbon in SCOD removal. During this first GAC run, SCOD in the influent averaged 690 mg/L for 17 samples and ranged from 422-1050 mg/L.

Some operational problems were experienced periodically in this first GAC run. During the period 9/11 to 9/25, the carbon columns were occasionally started and stopped because of process difficulties experienced in both of the pretreatment technologies (clarification and filtration). By 9/25 the majority of the operating problems were corrected; however, it was still necessary to start and stop the GAC system on several occasions as shown in Table 34 through the remainder of the run (10/12). Appendix D, Table D-33 presents the carbon column pressure readings that were taken periodically through the pilot study. During Run No. 1 (Days 19-36 in Table D-33) the carbon columns were operated in the downflow mode and the influent and effluent pressure readings across each of the four columns were monitored. Pressure drop increased with time; for example, on Day 19 (9/25), pressure drop across the first carbon column was only 0.07 kg/cm^2 (1 psi). By Day 23 (9/29), pressure drop had increased to 0.8 kg/cm^2 (12 psi) as a result of suspended solids buildup in the bed. At this point in time, the selected flow rate could no longer be maintained and the system was shut down and backwashed. Backwashing was required on four separate occasions, 9/29, 10/1, 10/4 and 10/8. About 10-15 minutes of backwash per column was generally required to free the carbon bed of the entrapped suspended material. Service water served as the source of backwash throughout the study. Pressure readings were taken immediately after backwash of the

TABLE 34. - GRAB SAMPLE DATA SUMMARY - GRANULAR ACTIVATED CARBON RUN #1

Date	Volume Treated		Cumulative Volume Treated		Flow Rates		SCOD, mg/L									Comments
	liters	gal	liters	gal	L/min	gal/min	M1	M2	M3	M4	M5	M6	M7	M8	M9	
9/11/84			0	0	-	-	Start GAC System									
	1048	277	1048	277	4.2	1.10	851	170	138	212	119	106	111	93	95	
9/11-25	3653	965					Operated Intermittently									
9/25/84	-	-	4699	1242	-	-										
9/26/84	5933	1567	10632	2809	4.2	1.1	626	404	209	148	92	108	98	71	66	
9/27/84	6461	1707	17093	4516	4.9	1.3	710	530	418	281	191	145	128	116	123	GAC Stopped Overnight
9/28/84	5638	1489	22731	6005	3.8	1.0	422	340	229	219	159	124	84	50	53	GAC Stopped Overnight
9/29/84	7702	2035	30432	8040	5.7	1.5	687	617	533	425	366	278	211	210	175	GAC Off 30 Min
9/30/84	8335	2202	38766	10242	6.1	1.6	645	499	373	277	198	174	168	142	146	GAC Off 78 Min
10/01/84	9489	2507	48255	12749	6.8	1.8	665	556	504	402	404	223	203	168	123	
10/02/84	10901	2880	59156	15629	7.6	2.0	651	499	326	662	179	469	402	281	214	GAC Off 100 Min
10/03/84	9572	2529	68728	18158	6.8	1.8	575	519	476	474	409	474	300	281	212	
10/04/84	9288	2454	78016	20612	6.8	1.8	602	637	632	551	424	279	309	192	232	
10/05/84	9136	2414	87153	23026	6.8	1.8	654	474	451	328	229	412	245	252	354	GAC Off 75 Min
10/06/84	11472	3031	98626	26057	6.8	1.8	632	558	571	520	390	387	250	340	121	
10/07/84	7653	2022	106279	28079	5.7	1.5	-	-	-	-	-	-	-	-	-	
10/08/84	8406	2221	114686	30300	6.4	1.7	866	948	987	788	759	564	701	409	302	
10/09/84	8516	2250	123202	32550	6.4	1.7	1050	866	866	1030	866	776	546	469	392	
10/10/84	9008	2380	132210	34930	6.4	1.7	710	591	679	564	554	361	375	305	512	
10/11/84	7290	1926	139500	36856	5.3	1.4	637	673	599	559	451	417	349	275	192	
10/12/84	8459	2235	147959	39091	5.7	1.5	747	645	698	894	570	517	451	397	298	
Avg					6.5	1.6	690									

NOTE: M1 is the GAC influent.
M2 is the Column No. 1 midpoint.
M3 is the Column No. 1 effluent.
M4 is the Column No. 2 midpoint.
M5 is the Column No. 2 effluent.
M6 is the Column No. 3 midpoint.
M7 is the Column No. 3 effluent.
M8 is the Column No. 4 midpoint.
M9 is the Column No. 4 effluent.

Backwash Events
9/29/84 Backwash at 8270 gal
10/01/84 Backwash at 13610 gal
10/04/84 Backwash at 21108 gal
10/08/84 Backwash at 30670 gal

carbon columns. The backwash was very effective in removing the headloss causing material. For each of the four backwashes performed in Run No. 1, pressure readings returned to their original headloss settings following return of the bed to service.

Backwash did, however, have an effect on the effluent SCOD concentrations based on daily sample analytical values. Figure 94 has been prepared to better illustrate this point. This figure presents a plot of SCOD concentration versus date. Each of the four backwashing events previously described has been shown. Notice on Figure 94 that effluent SCOD concentrations (M3-M9) sharply fluctuated following a backwash. Between backwashes, the effluent SCOD values drop back to their previous levels. This sharp fluctuation in effluent SCOD following backwash would not normally be expected. It is probable that due to the inadequacy of the carbon backwash system (previously discussed in detail in Section 5), proper stratification of the carbon bed was never achieved during the initial washing of fines from the carbon columns prior to system start-up. As a result, some restratification of the carbon bed occurred with each subsequent backwash, causing fluctuations in effluent SCOD concentration. Because the analytical data were not representative of a well designed and operated carbon adsorption system, SCOD breakthrough curves were not plotted for the GAC grab sample data.

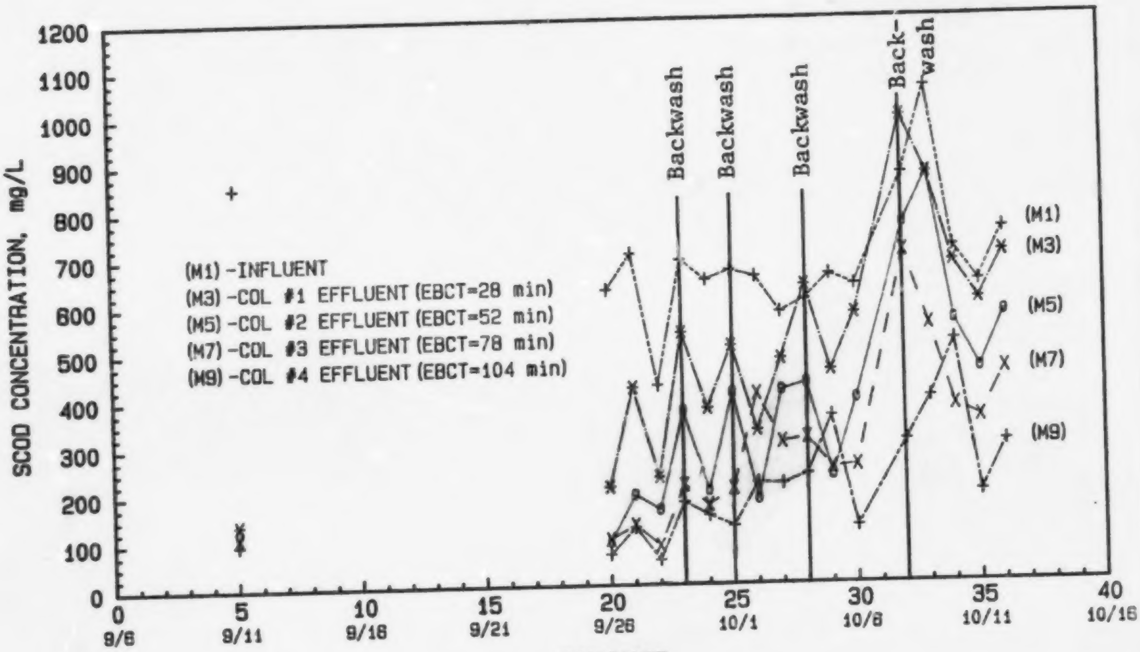


Figure 94. Fluctuation in SCOD Resulting From Backwash.

GAC Run No. 1 Composite Sample Results

As discussed previously, composite samples were also collected over 24 hours of operation from the GAC influent (sample point M) and effluent (sample point N) and analyzed for selected parameters. A comparison of influent and effluent analytical values for Run No. 1 is presented in Appendix D, Tables D-32 and D-34. Daily percent removals were also determined and are shown in these tables. A summary of these tables is presented in Table 35. Suspended solids removal for eighteen comparative data points averaged 59 percent. The TBOD removal was about 52 percent and the TCOD removal was 69 percent. Seventy-one percent of the SCOD was removed during the study. Figures 95 and 96 present a graphical comparison of influent and effluent TSS and TBOD.

Table 36 has been prepared so that influent and effluent composite SCOD values can be compared to the cumulative volume processed through the GAC. Similar to the grab sample operation data summary previously presented in Table 34, the flow rate and cumulative volume processed is shown for each composite sampling period.

The composite influent SCOD averaged 691 mg/L for the 17 samples collected during GAC Run No. 1. This compares very well to the 690 mg/L SCOD average for the grab samples. Influent and effluent SCOD versus volume processed is illustrated on Figure 97. Although effluent SCOD increased with the amount of wastewater passed through the GAC, it is evident from reviewing Figure 97 that total exhaustion of the carbon was not reached. The amount of SCOD adsorbed by the carbon was previously shown in Table 36. During this first run, 68.6 kg (151.5 lb) of SCOD was removed on the GAC based on the 24 hour composite results.

TABLE 35. ACTIVATED CARBON RUN NO. 1 REMOVAL EFFICIENCY* (9/11-10/12)

Parameter	Influent**	Effluent***	% Removal
TSS, mg/L	170	69	59 (18)
TBOD, mg/L	58	28	52 (7)
TCOD, mg/L	879	275	69 (17)
SCOD, mg/L	691	199	71 (17)

*The influent/effluent comparison was made only when both values were available. Only composite values are compared.

**Influent TBOD samples were taken from sample point "L" and TSS, TCOD and SCOD samples were taken from sample point "M". Average values for entire run.

***Effluent from sample point "N". Average values for entire run.

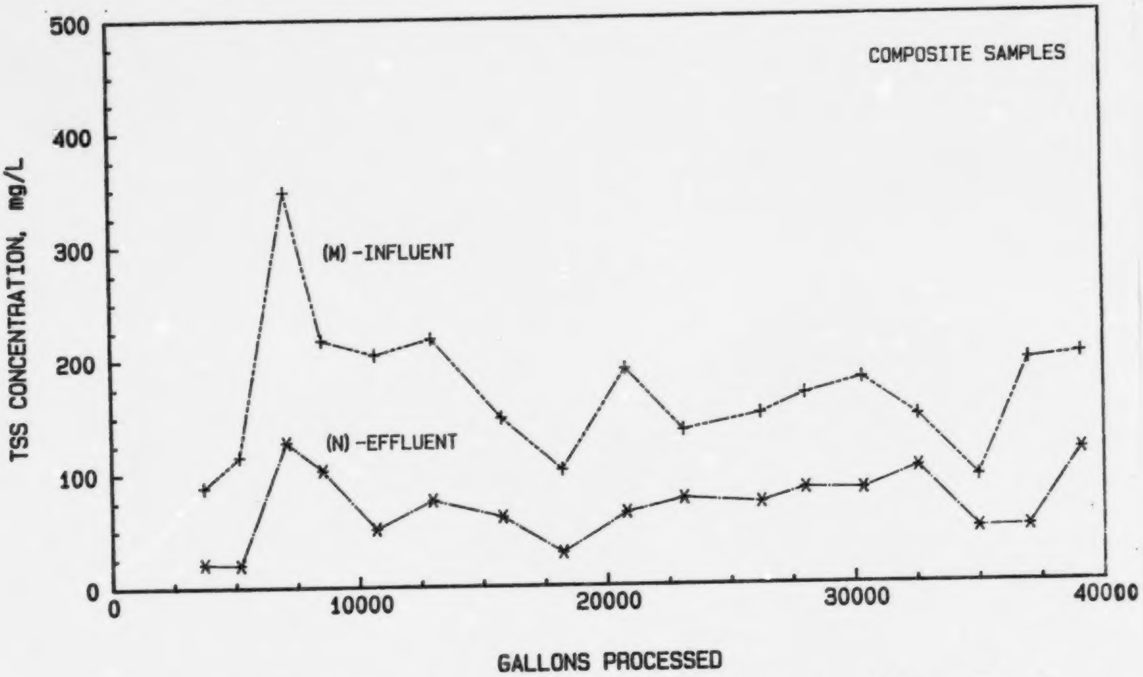


Figure 95. Influent and Effluent TSS Values for GAC Run No. 1.

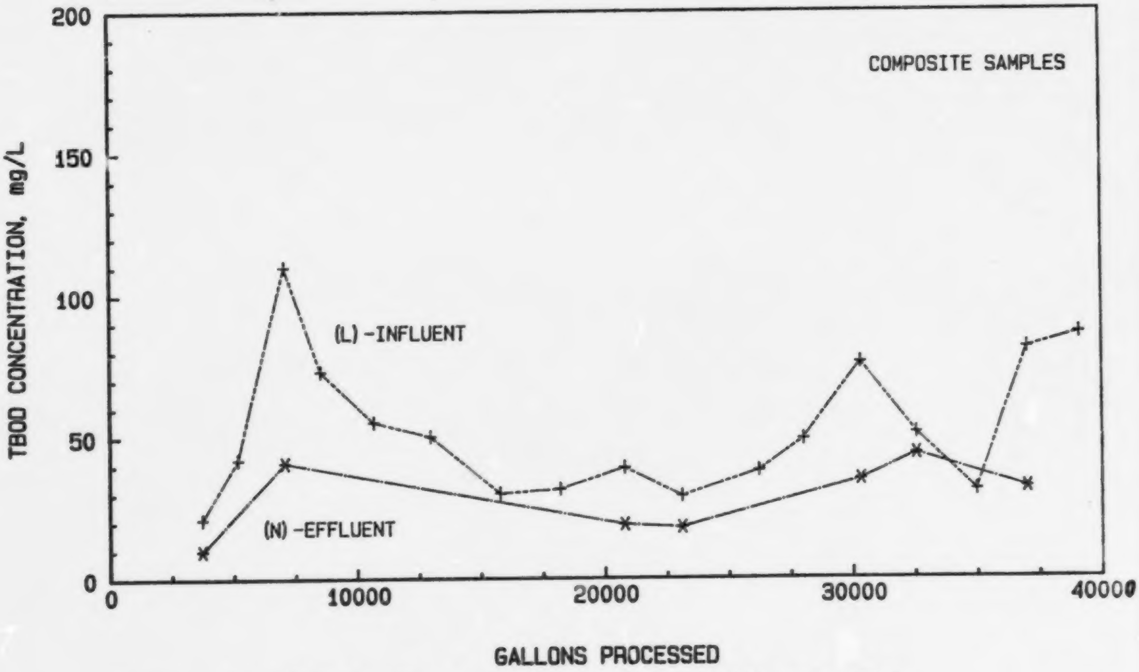


Figure 96. GAC Run No. 1 Influent Versus Effluent TBOD Concentration.

TABLE 36. GRANULAR ACTIVATED CARBON SCOD (COMPOSITE SAMPLE) SUMMARY - Run No. 1

Date	Volume Treated		Cumulative Volume Treated		Flow Rate		SCOD mg/L		% SCOD Removed	SCOD Removed	
	liters	gal	liters	gal	L/min	gal/min	M	N		kg	lb
09/11	0	0	0	0			Start GAC				
09/11-09/25	8857	2340	8857	2340							
09/25-09/26	5246	1586	14103	3726	3.8	1.0	632	88	86.1	2.9	6.3
09/26-09/27	5496	1452	19599	5178	4.2	1.1	575	112	80.5	2.5	5.6
09/27-09/28	7203	1903	26802	7081	4.9	1.3	654	134	79.5	3.8	8.3
09/28-09/29	5541	1464	32343	8545	3.8	1.0	637	177	72.2	2.5	5.6
09/29-09/30	8073	2133	40416	10678	5.7	1.5	583	148	74.6	3.5	7.7
09/30-10/01	8683	2294	49099	12972	6.1	1.6	632	102	83.9	4.6	10.1
10/01-10/02	10628	2808	59727	15780	6.8	1.8	926	93	90.0	8.9	19.5
10/02-10/03	9194	2429	68921	18209	6.8	1.8	588	261	55.6	3.0	6.6
10/03-10/04	9663	2553	78584	20762	6.8	1.8	676	192	71.6	4.7	10.3
10/04-10/05	8868	2343	87452	23105	6.1	1.6	572	236	58.8	3.0	6.6
10/05-10/06	11809	3120	99262	26225	6.8	1.8	628	251	60.0	4.5	9.8
10/06-10/07	6779	1791	106041	28016	5.3	1.4	809	371	54.1	3.0	6.5
10/07-10/08	8736	2308	114776	30324	6.4	1.7	957	281	70.6	5.9	13.0
10/08-10/09	8425	2226	123202	32550	6.1	1.6	860	283	67.0	4.9	10.7
10/09-10/10	9167	2422	132369	34972	6.4	1.7	659	238	63.9	3.9	8.5
10/10-10/11	7695	2033	140064	37005	5.3	1.4	578	142	75.4	3.9	7.4
10/11-10/12	7896	2086	147959	39091	5.3	1.4	779	321	58.8	3.6	8.0
Avg.							691				

Note: Sample Point M is the GAC Influent.
Sample Point N is the GAC Effluent.

GAC Run No. 2 Grab Sample Results

After completion of the first run, the spent carbon depth was measured and the carbon was unloaded from each column. It was decided to conduct Run No. 2 in the upflow, expanded bed mode. The system was repiped, as necessary, to accomodate upflow operation. It was also decided to install a gravel/sand support media on the bottom of each column to assist in flow distribution. After the support media was in place, fresh carbon was installed and the columns were backwashed to remove the fines. Addition of the gravel/sand support reduced the effective carbon bed height in each column by over 30.4 cm (12 in.). Thus, the flow rate selected for Run No. 2 was less than that used in Run No.1. The GAC system operated almost problem free during the second run. On only one occasion (12/1-2) the system was shut down because of a pump problem. Flow was maintained relatively constant during the Run No. 2 and no backwashing was required. Samples were collected similar to that discussed above for Run No. 1 except that the daily midpoint grab samples from each column were eliminated.

The second GAC run was conducted over 42 days of operation. Testing commenced on October 24 and continued until December 4. During this period, 199,830 liters (52,795 gallons) of pharmaceutical plant effluent were treated by GAC. Prior to the GAC, the wastewater was chemically treated, clarified and filtered. For this run, the empty bed contact time was increased to 140 minutes total or 35 minutes per column compared to 104

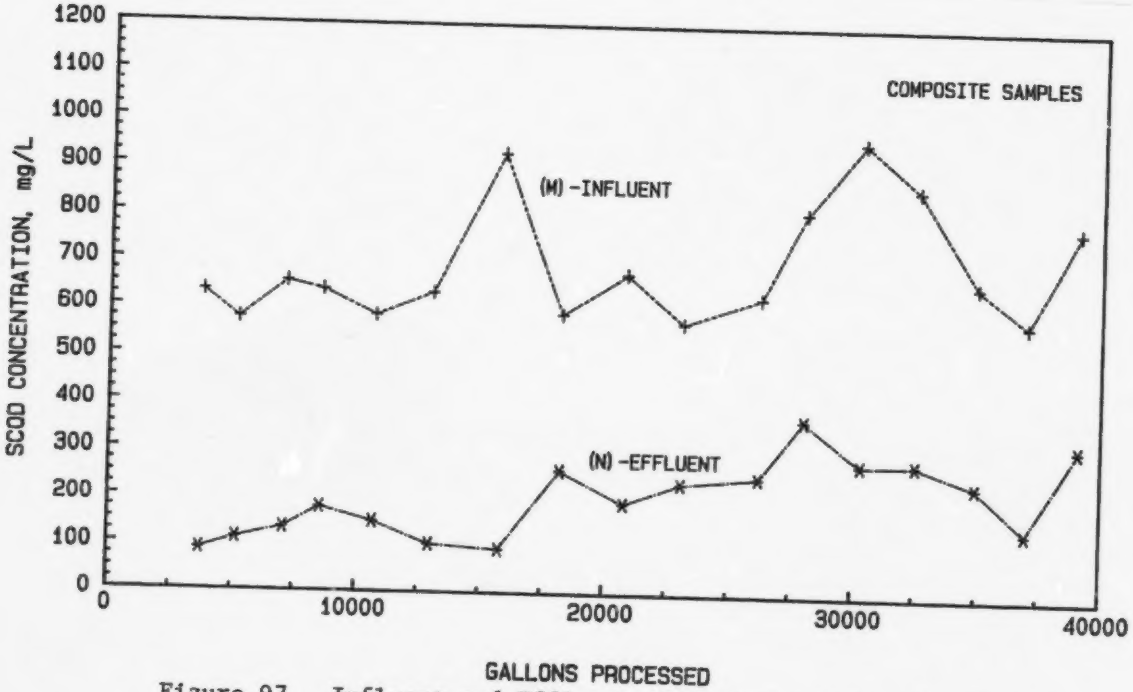


Figure 97. Influent and Effluent SCOD Versus Volume Processed.

minutes total for the first GAC run. To obtain the increased contact time, the hydraulic rate was decreased to 36.7 l/min-m^2 (0.9 gpm/ft^2).

Similar to GAC Run No. 1, records were kept regarding the volume of wastewater that had passed through the carbon at the time of grab sampling. The daily volume of water treated in addition to the grab sample SCOD analytical results are summarized in Table 37. As can be seen by reviewing Table 37, samples were collected each day during the study from the influent and each of the carbon column effluents. Pressure readings were taken for Run No. 2 from Days 66 to 89 (11/11 - 12/4). The pressure drop observed during the study was minimal. The information that was generated from the study and tabulated in Table 37 was used as the basis for determining the efficiency of SCOD removal by the GAC system.

To better illustrate the capability of the GAC to adsorb organic impurities as measured by SCOD, several breakthrough curves were prepared and are shown in the Appendix D as Figures D-15 to D-19. A separate figure has been prepared for each column effluent. Breakthrough is defined as the processing time on the column exhaustion curve when the impurity concentration in any of the carbon column effluents is no longer acceptable. From each curve the time and volume processed to reach a SCOD breakthrough of 300, 400 and 500 mg/L was calculated. A summary of these calculations is shown in Table 38. Also shown in Table 38 is the cumulative residence time, carbon weight and carbon depth. Note that the influent SCOD concentration averaged 662 mg/L for the 42 daily samples that were collected and ranged from 449 mg/L to 926 mg/L.

The carbon usage rate in kilograms per 1000 liters or pounds per 1000 gallons can be determined by dividing the weight of carbon in each column by the volume processed to breakthrough. Table 39 presents a summary of carbon usage rates. This table indicates that carbon usage decreases with an increase in allowable effluent SCOD concentration. The carbon usage to maintain an effluent SCOD concentration of 300 mg/L or less decreased from 3.1 to 2.1 kg/1000 liters as EBCT was increased from 35 to 140 minutes, respectively; for a 400 mg/L or less SCOD effluent, the carbon usage ranged from 2.6 to 1.7 kg/1000 liters and for a 500 mg/L or less effluent SCOD, the carbon usage ranged from 1.9 to 1.2 kg/1000 liters as the EBCT was increased from 35 to 140 minutes, respectively.

GAC Run No. 2 Composite Sample Results

Daily 24 hour composite samples were collected for GAC Run No. 2 from 10/24 - 12/4. These samples of GAC influent and final effluent were analyzed for suspended solids, TBOD, TCOD and SCOD. The daily analytical results for suspended solids, pH, turbidity, temperature and TBOD are shown in Tables D-32 and D-35, Appendix D. A summary of percent removals is presented in Table 40. Suspended solids removal averaged only 14 percent for the 38 analyses performed. The TBOD removal was less than 30 percent. TBOD and TSS influent and effluent results are plotted on Figures 98 and 99, respectively. It should be pointed out that the averages in Table 40 are for the entire run and not to some specific effluent SCOD concentration.

TABLE 37. SCOD GRAB SAMPLE DATA SUMMARY - GAC RUN NO. 2

Date	Volume Treated		Cumulative Volume Treated		Flow Rate		SCOD, mg/L				
	liters	gal	liters	gal	L/min	gal/min	M1	M3	M5	M7	M9
10/24/84	0	0	0	0	0	0	Start	GAC	System		
10/25/84	2816	744	2816	744	3.2	0.85	670	83	83	85	68
10/26/84	3698	977	6514	1721	2.0	0.53	718	146	108	106	108
10/27/84	3494	923	10008	2644	3.4	0.90	712	136	132	95	81
10/28/84	4731	1250	14739	3894	3.4	0.90	833	236	153	143	146
10/29/84	5723	1512	20462	5406	3.2	0.84	926	434	259	307	247
10/30/84	3683	973	24145	6379	3.3	0.87	836	375	194	127	102
10/31/84	4667	1233	28812	7612	3.0	0.88	718	610	214	151	119
11/01/84	4720	1247	33532	8859	3.2	0.85	693	614	203	190	133
11/02/84	4349	1149	37881	10008	2.8	0.74	578	474	214	170	127
11/03/84	4122	1089	42003	11097	3.0	0.80	575	476	198	108	93
11/04/84	4599	1215	46602	12312	3.3	0.87	523	469	252	114	110
11/05/84	4576	1209	51178	13521	3.2	0.84	836	693	456	241	184
11/06/84	4807	1270	55985	14791	3.3	0.88	916	776	580	323	216
11/07/84	5007	1323	60992	16114	3.1	0.83	788	556	422	354	250
11/08/84	4709	1244	65701	17358	3.7	0.97	759	718	523	375	216
11/09/84	5413	1430	71114	18788	3.7	0.99	662	645	492	373	234
11/10/84	5496	1452	76610	20240	3.8	1.0	830	827	718	604	397
11/11/84	4708	1244	81318	21484	3.3	0.88	718	607	591	461	241
11/12/84	5859	1548	87177	23032	3.7	0.97	656	764	554	476	212
11/13/84	4905	1296	92082	24328	3.7	0.97	629	618	479	412	245
11/14/84	5307	1402	97389	25730	3.7	0.98	710	651	557	486	330
11/15/84	5427	1434	102816	27164	3.6	0.96	652	629	596	492	387
11/16/84	5053	1335	107869	28499	3.7	0.97	747	549	583	535	356
11/17/84	5662	1496	113531	29995	3.6	0.96	528	520	412	250	236
11/18/84	4921	1300	118452	31295	3.7	0.97	610	605	554	499	308
11/19/84	5564	1470	124016	32765	3.6	0.95	538	494	456	314	402
11/20/84	5185	1370	129201	34135	3.6	0.96	451	429	351	356	247

(continued)

TABLE 37. (continued)

Date	Volume Treated liters	Volume Treated gal	Cumulative Volume Treated liters	Cumulative Volume Treated gal	Flow Rate L/min	Flow Rate gal/min	SCOD, mg/L M1	M3	M5	M7	M9
11/21/84	5477	1447	134678	35582	4.0	1.05	512	476	385	340	278
11/22/84	5250	1387	139928	36969	3.8	1.00	551	482	469	328	259
11/23/84	5746	1518	145674	38487	3.8	1.01	499	497	427	378	351
11/24/84	6082	1607	151756	40094	3.7	0.98	449	446	397	328	295
11/25/84	5110	1350	156866	41444	3.8	1.00	469	476	419	328	316
11/26/84	4750	1255	161616	42699	3.7	0.98	482	446	356	314	261
11/27/84	5352	1414	166968	44113	3.6	0.94	502	632	412	333	275
11/28/84	5098	1347	172066	45460	3.5	0.92	551	476	471	373	328
11/29/84	4943	1306	177009	46766	3.5	0.92	854	812	715	632	523
11/30/84	5322	1406	182331	48172	3.5	0.93	570	525	479	424	422
12/01/84*	4686	1238	187017	49410	3.5	0.93	575	551	494	469	387
12/02/84	2487	657	189504	50067	3.8	1.00	744	578	498	375	305
12/03/84	2101	555	191605	50622	2.7	0.70	707	632	556	417	385
12/04/84	5511	1456	197116	52078	3.8	1.01	767	715	715	602	484
12/04/84	2714	717	199830	52795	3.9	1.02	761	718	634	556	525
Avg							662				

* Carbon columns off 1617 hours (12/1/84) to 1550 hours (12/2/84) - pump problems.

Note: M1 is the GAC influent
M3 is the Column No. 1 effluent
M5 is the Column No. 2 effluent
M7 is the Column No. 3 effluent
M9 is the Column No. 4 effluent

TABLE 38. GAC RUN NO. 2 GRAB SAMPLE DESIGN DATA

GAC Col. No.	GAC Column Location	GAC Sample Point	Cumulative Residence* Time, Min.	Cumulative Carbon Weight, kg	Cumulative Depth of Carbon m	Processing Volume at Breakthrough, liter (gal) SCOD=300 mg/L	SCOD=400 mg/L	SCOD=500 mg/L
1	Influent	M1	0	0		0	0	0
1	Effluent	M3	35	51.4	1.3	16,590(4,380)	19,480(5,150)	26,630(7,040)
2	Effluent	M5	70	102.7	2.6	47,680(12,600)	49,920(13,190)	52,880(13,970)
3	Effluent	M7	105	154.1	3.8	54,640(14,440)	74,250(19,620)	103,760(27,410)
4	Effluent	M9	140	206	5.1	95,520(25,240)	123,900(32,730)	176,430(46,610)

Note: Influent Average SCOD=662 mg/l (42 Data Points)
Influent Range of SCOD=449-926 mg/l (42 Data Points)

* At a flow rate of 37 l/min/m^2 (0.9 gpm/ft^2).

TABLE 39. CARBON USAGE REQUIREMENTS

Column No.	Carbon Usage, kg/1000 L (lb/1000 gal) SCOD=300 mg/L	SCOD=400 mg/L	SCOD=500 mg/L
1	3.1 (25.8)	2.6 (21.9)	1.9 (16.0)
2	2.1 (17.9)	2.1 (17.1)	1.9 (16.2)
3	2.8 (23.5)	2.1 (17.3)	1.5 (12.4)
4	2.1 (17.9)	1.7 (13.8)	1.2 (9.7)

Each day during the GAC Run No. 2 study, the time and cumulative flow totalizer readings were recorded at the time of composite sampling. This information is shown in Table 41 along with the volume treated, flow rate and SCOD results. For the 42 samples collected, SCOD in the influent averaged 651 mg/L. This compares quite favorably to the 662 mg/L SCOD average obtained from the grab samples.

The daily influent and effluent SCOD values are plotted in the form of breakthrough curves on Figure 100. The daily amount of SCOD removed from the wastewater is tabulated in Table 41.

The information presented in Table 41 and on Figure 100 were used to prepare carbon usage estimates based on the composite sample results. Table 42 presents the processing volume, processing time and carbon usage rates for SCOD effluent concentrations of 300, 400 and 500 mg/L. Comparing the carbon usage requirements based on the composite sample results to the grab results previously shown in Table 39, it is evident that some differences exist. For a SCOD effluent design of 300 mg/L, carbon usage rate is quite similar; however, the carbon usage rates for the 400 and 500 mg/L effluent SCOD are less for the composite sample results than they are for the grab sample study. It must be remembered that the grab sample data are based on a single point in time as opposed to the composite results which represent the average effluent concentration over a 24 hour period.

Specific organic 24 hour composite samples were collected manually (grab every 3 hours) four times during the study from the GAC influent and GAC effluent. The sampling dates were November 6, November 20, November 27 and December 4. The purpose of this study was to identify and measure the specific organic compounds present in the GAC influent and evaluate efficiency of removal by activated carbon. Only two sets of the composite sample influents and effluents were analyzed (11/20 and 12/4) and these results are discussed in Section 10.

TABLE 40. ACTIVATED CARBON RUN NO. 2 REMOVAL EFFICIENCY* (10/24 - 12/4/84)

Parameter	Influent** mg/L	Effluent*** mg/L	% Removal
TSS	87	75	14 (38)
TBOD	121	> 85	<30 (14)
TCOD	914	432	53 (42)
SCOD	651	251	61 (42)

* The influent/effluent comparison was made only when both values were available. Averages are for entire run.

** Influent TBOD was taken from sample point "L," TSS, TCOD, and SCOD were taken from sample point "M". Average values for entire run.

*** Effluent from sample point "N". Average values for entire run.

( ) Indicates number of data points used to obtain average.

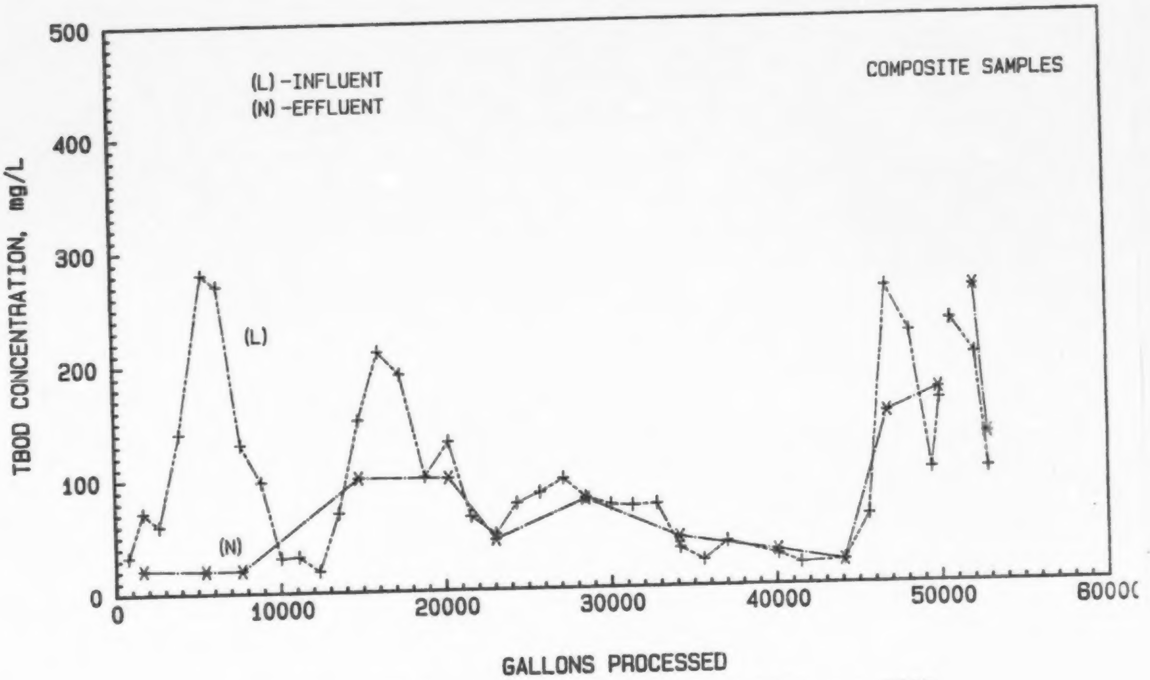


Figure 98. GAC Run No. 2 Influent and Effluent TBOD Concentrations.

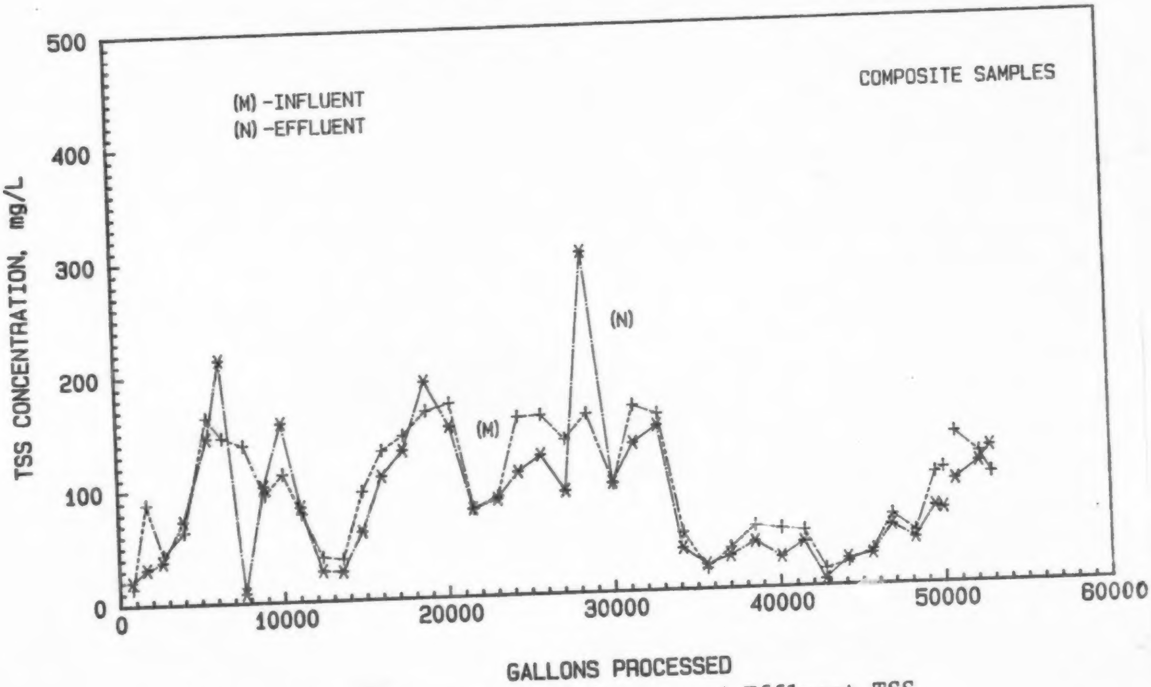


Figure 99. GAC Run No. 2 Influent and Effluent TSS Concentrations.

TABLE 41. GRANULAR ACTIVATED CARBON COMPOSITE SAMPLE DATA SUMMARY - RUN NO. 2

Date	Volume Treated		Cumulative Volume Treated		Flow Rate		SCOD mg/L		% SCOD Removed	SCOD Removed	
	liters	gal	liters	gal	L/min	gal/min	M	N		kg	lb
Started 10/24											
10/24-10/25	2816	744	2816	744	3.4	0.9	637	71	88.9	1.6	3.5
10/25-10/26	3490	922	6306	1666	2.6	0.7	744	98	86.8	2.3	5.0
10/26-10/27	3702	978	10008	2644	2.6	0.7	679	64	90.6	2.3	5.0
10/27-10/28	4856	1283	14864	3927	3.4	0.9	818	75	90.8	3.6	8.0
10/28-10/29	5753	1520	20617	5447	3.0	0.8	1020	185	81.9	4.8	10.6
10/29-10/30	3528	932	24145	6379	3.4	0.9	882	115	87.0	2.7	6.0
10/30-10/31	4826	1275	28971	7654	3.4	0.9	866	127	85.3	3.6	7.9
10/31-11/01	4648	1228	33619	8882	3.4	0.9	750	144	80.8	2.8	6.2
11/01-11/02	4296	1135	37915	10017	2.6	0.7	604	148	75.5	2.0	4.3
11/02-11/03	4088	1080	42003	11097	3.0	0.8	588	123	79.1	1.9	4.2
11/03-11/04	4652	1229	46655	12326	3.4	0.9	572	106	81.5	2.2	4.8
11/04-11/05	4591	1213	51246	13539	3.0	0.8	659	144	78.1	2.4	5.2
11/05-11/06	4739	1252	55985	14791	3.4	0.9	910	70	92.3	4.0	8.8
11/06-11/07	4750	1255	60735	16046	3.0	0.8	830	254	69.4	2.7	6.0
11/07-11/08	4966	1312	65701	17358	3.8	1.0	690	305	55.8	1.9	4.2
11/08-11/09	5413	1430	71114	18788	3.8	1.0	681	302	55.7	2.1	4.5
11/09-11/10	5496	1452	76610	20240	3.8	1.0	712	279	60.8	2.4	5.2
11/10-11/11	4932	1303	81542	21543	3.4	0.9	741	284	61.7	2.3	5.0
11/11-11/12	5636	1489	87178	23032	3.8	1.0	681	347	49.0	1.9	4.2
11/12-11/13	4905	1296	92083	24328	3.8	1.0	715	247	65.5	2.3	5.1
11/13-11/14	5307	1402	97390	25730	3.8	1.0	688	235	65.8	2.4	5.3
11/14-11/15	5378	1421	102768	27151	3.8	1.0	707	354	49.9	1.9	4.2
11/15-11/16	5061	1337	107829	28488	3.8	1.0	563	373	33.7	1.0	2.1
11/16-11/17	5704	1507	113533	29995	3.8	1.0	676	286	57.7	2.2	4.9
11/17-11/18	4921	1300	118454	31295	3.8	1.0	632	293	53.6	1.7	3.7
11/18-11/19	5564	1470	124018	32765	3.8	1.0	591	293	50.4	1.7	3.7
11/19-11/20	5185	1370	129203	34135	3.8	1.0	499	284	43.1	1.1	2.5

(continued)

TABLE 41. (continued)

Date	Volume Treated		Cumulative Volume Treated		Flow Rate		SCOD mg/l		% SCOD Removed	SCOD Removed	
	liters	gal	liters	gal	L/min	gal/min	M	N		kg	lb
11/20-11/21	5382	1422	134585	35557	3.8	1.0	487	250	48.7	1.3	2.8
11/21-11/22	5431	1435	140016	36992	3.8	1.0	512	212	58.6	1.6	3.6
11/22-11/23	5715	1510	145731	38502	3.8	1.0	422	259	38.6	1.0	2.1
11/23-11/24	5988	1582	151719	40084	3.8	1.0	397	192	51.6	1.2	2.7
11/24-11/25	5185	1370	156904	41454	3.8	1.0	375	265	29.3	0.6	1.3
11/25-11/26	4789	1260	161693	42714	3.8	1.0	351	192	45.3	0.8	1.7
11/26-11/27	5197	1373	166890	44087	3.8	1.0	397	216	45.6	1.0	2.1
11/27-11/28	5651	1493	172541	45580	3.4	0.9	466	254	45.5	1.2	2.7
11/28-11/29	4557	1204	177098	46784	3.4	0.9	833	466	44.1	1.7	3.7
11/29-11/30	5254	1388	182352	48172	3.4	0.9	687	449	34.6	1.3	2.8
11/30-12/01	4686	1238	187038	49410	3.4	0.9	578	489	15.4	0.4	0.9
12/01/12/02*	1938	512	188976	49922	3.8	1.0	517	387	25.1	0.2	0.5
12/02-12/03	2752	727	191728	50649	2.6	0.7	684	330	51.8	1.0	2.2
12/03-12/04	5484	1449	197212	52098	3.8	1.0	750	461	38.5	1.6	3.5
12/04-12/04	2638	697	199850	52795	3.8	1.0	761	499	34.4	0.7	1.5
Avg							651				

*Carbon columns off 1617 hrs (12/1/84) to 1550 hrs (12/2/84) - pump problems.

Note: Sample point M is the GAC influent.
Sample point N is the GAC effluent.

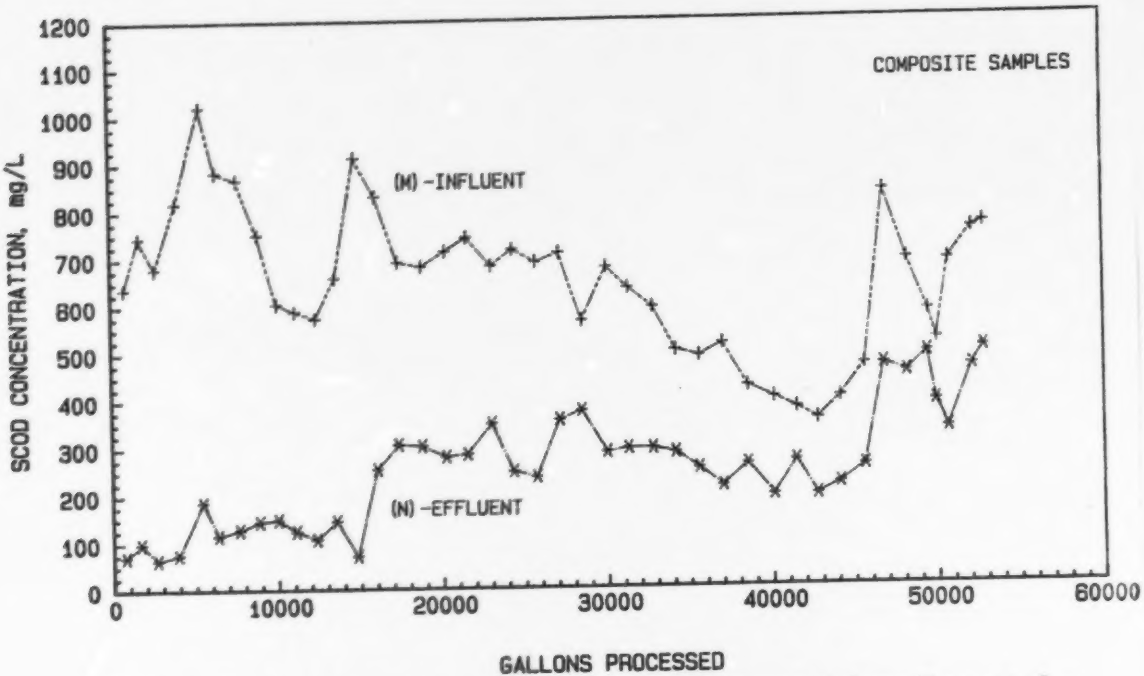


Figure 100. Influent and Effluent SCOD Versus Volume Processed - GAC Run No. 2 Composites.

TABLE 42. GAC RUN NO. 2 COMPOSITE SAMPLE DESIGN DATA

Parameter	Targeted Effluent SCOD		
	300 mg/L	400 mg/L	500 mg/L
Processing Volume at Breakthrough, liters	65,490	175,680	199,850
gallons	17,305	46,415	52,800
Processing Time at Breakthrough, hrs	320	860	978
Carbon Usage, kg/1000 L	3.1	1.2	1.0
lb/1000 gal	26.0	9.7	8.5

SECTION 10

SPECIFIC ORGANIC COMPOUNDS

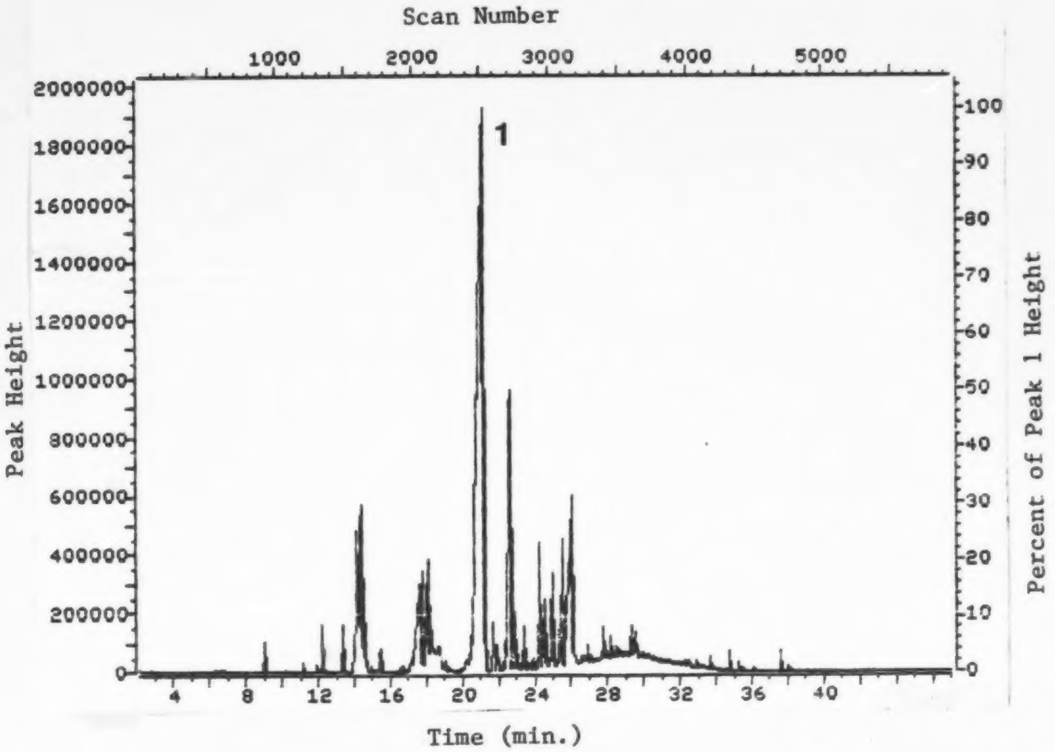
BIOLOGICAL EFFLUENT ORGANICS

In order to identify the specific organic constituents in the pharmaceutical plant effluent, a series of mass spectral and infrared studies was carried out by several laboratories. A grab composite sample of biologically treated pharmaceutical plant effluent was collected on March 14 (EPA Sample Pharm 26) using a 50:50 mix of the two final clarifier effluents. Split samples of this effluent sample were submitted to S-Cubed (San Diego, CA), the EPA Athens laboratory (Athens, GA) and ESE (Gainesville, FL) for gas chromatography/mass spectrometry (GC/MS) low resolution analysis using the standard EPA 625 extraction method. Approximately 17 peaks were observed by each of the laboratories.

An extract of a composite sample made of the control pilot plant effluent collected from October 17 to 21 (ESE Sample 435602) resulted in a chromatogram with approximately 9 out of the 17 major peaks having mass spectra similar to those determined from the March 14 samples. Figure 101 presents a total ion chromatogram of the control pilot plant effluent which is characterized by a large peak labeled No. 1. Figures 102 through 106 present detailed views of each segment of the total ion chromatogram of the pilot plant effluent extract with an "X" marking peaks having similar mass spectra in the March and October samples. Copies of the total ion chromatogram and the mass spectra of each peak for the ESE split sample are presented in Appendix F. The mass spectra of matching spectra from the EPA Athens laboratory split sample are also included in Appendix F for comparison. Matching spectra from the S-Cubed split sample are not included in Appendix F although these spectra did indeed match those spectra from the other two laboratories.

The EPA Athens laboratory also performed a series of high pressure liquid chromatography/mass spectroscopy (HPLC/MS) analyses which gave essentially the same distribution of compounds.

After consultation with the EPA Athens mass spectroscopy laboratory, a sample of the extract (obtained from the October 17-21 samples) was submitted to Triangle Laboratories, Inc., for high-resolution GC/MS using a high-resolution magnetic sector mass spectrometer (VG70-HS mass spectrometer from V.G. Instruments, Inc.) with a resolution of 3,000. Figure 107 presents the low resolution mass spectrum of Peak 1 along with the exact mass of the molecular ion peak as determined by the high-resolution MS. A



NOTES: Chromatographic Conditions

Column: 30 m x 0.5 mm O.D. x 0.32 mm I.D.
DB5 on fused silica (0.25-um film thickness)

Flow rate: 1 ml/min (helium)

Oven temperature program: isothermal at 30°C for 5 min then 8°C/min to 285°C and hold at 285°C for 11 min.

Injection: 2 ul
Injection temperature: 260°C

Figure 101. Total Ion Chromatogram (2 to 45 Minutes) Control Pilot Plant Effluent.

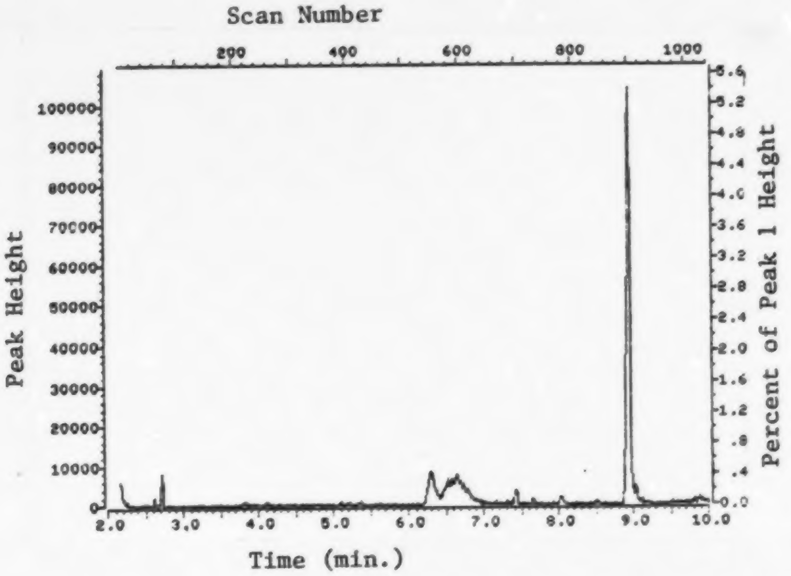


Figure 102. Total Ion Chromatogram (2 to 10 Minutes) Control Pilot Plant Effluent.

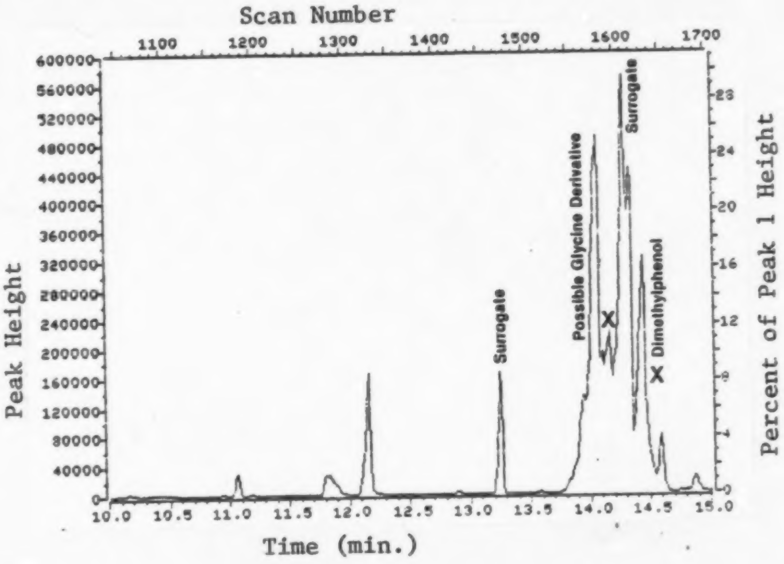


Figure 103. Total Ion Chromatogram (10 to 15 Minutes) Control Pilot Plant Effluent.

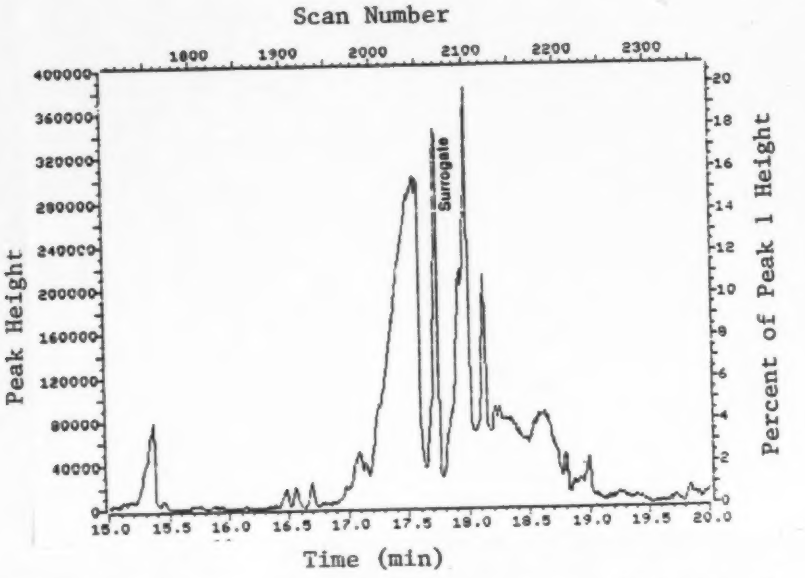


Figure 104. Total Ion Chromatogram (15 to 20 Minutes) Control Pilot Plant Effluent.

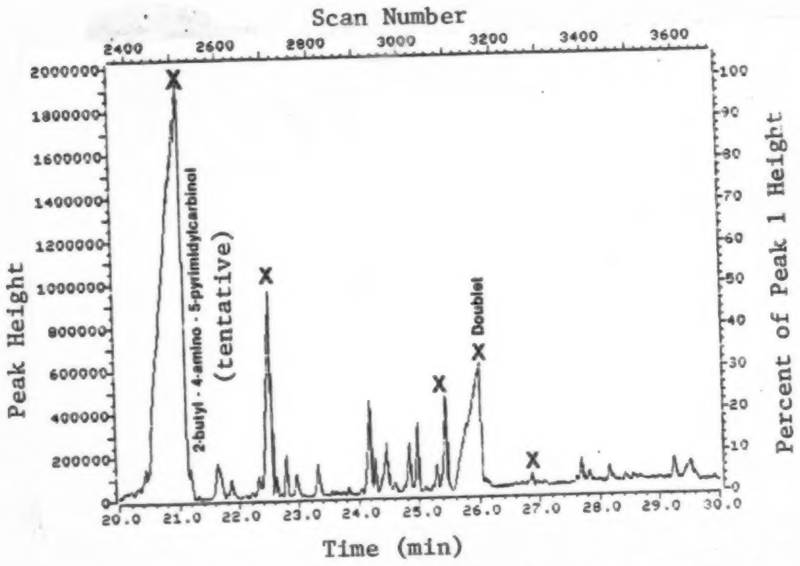


Figure 105. Total Ion Chromatogram (20 to 30 Minutes) Control Pilot Plant Effluent.

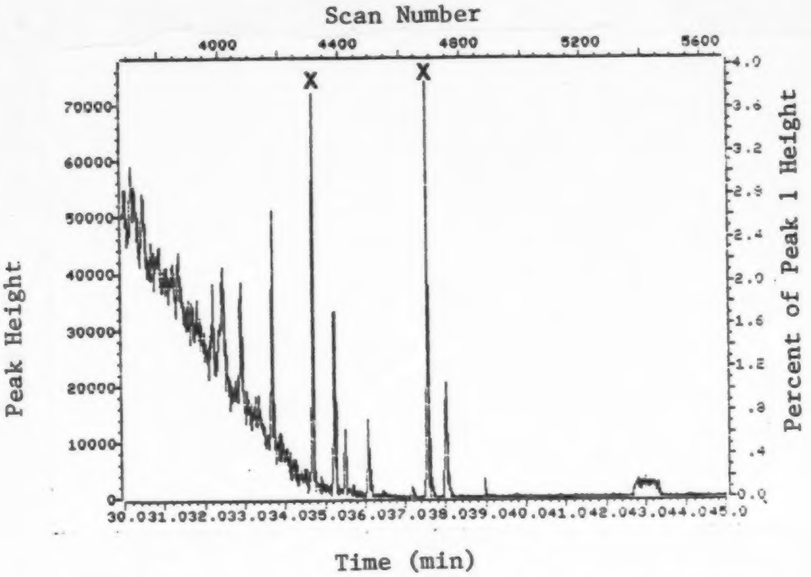


Figure 106. Total Ion Chromatogram (30 to 45 Minutes) Control Pilot Plant Effluent.

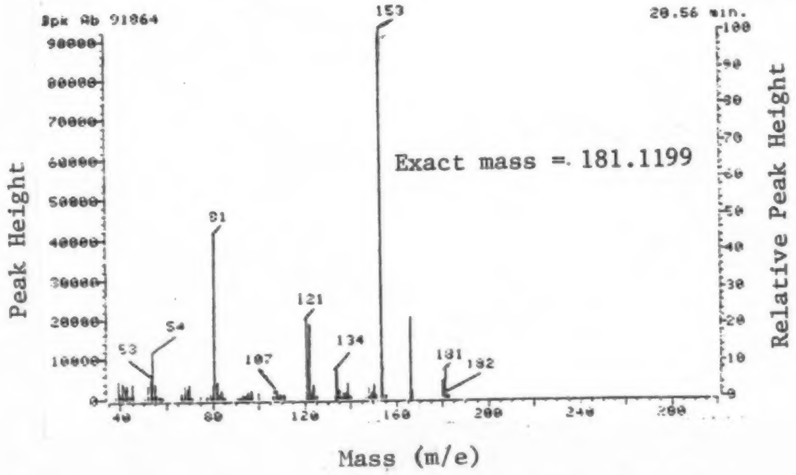


Figure 107. Low-Resolution Mass Spectrum of Peak 1 Control Pilot Plant Effluent.

sample of the same extract was also submitted to the University of Georgia Chemistry Department for gas chromatographic/Fourier transform infrared analysis (GC/FTIR). A copy of the infrared spectrum of Peak 1 is presented on Figure 108.

The EPA Athens laboratory identified dimethylphenol, which was confirmed by ESE's analysis (see Figure 103). However, computerized and manual spectrum analysis by the S-Cubed, EPA Athens, and ESE laboratories failed to provide an identification of any of the remaining compound structures. In the infrared spectrum of Peak 1 on Figure 108, the three infrared bands above 3,000 cm^{-1} indicated the presence of an amino group and the possible presence of an intramolecular hydrogen bonded -OH group. The principal IR bands were in wavenumbers (cm^{-1}) 3,460; 3,300; 3,160; 2,980; 2,950; 2,880; 2,780; 1,700; 1,540; 1,440 and 1,060.

Table 43 presents the mass spectral peak assignments of the molecular formula of each principal ion based upon the high-resolution mass spectrum. The standard deviation of the mass measurements as well as the theoretical mass for each ion are also presented. The lowest mass scanned by the high resolution MS was 90 m/e. These assignments account for all of the principal ions in the spectrum of Peak 1.

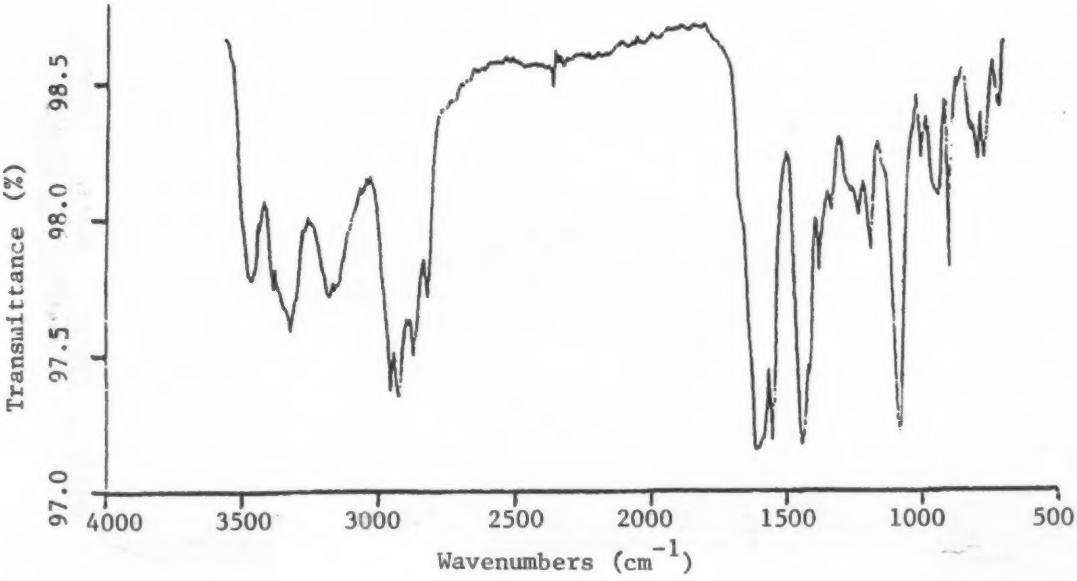
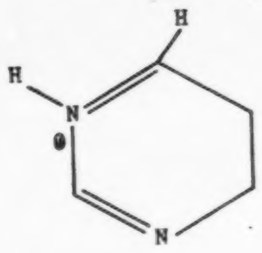


Figure 108. Infrared Spectrum of Peak 1 Control Pilot Plant Effluent.

The formula $C_9H_{15}N_3O$ was assigned to the molecular ion peak and has a degree of unsaturation of 4 and a molecular weight of 181. Amines commonly lose hydrogen atoms and give rise to a large M-1 ion, as observed for the 180 to 181 m/e peaks on Figure 107. The base peak at 153 m/e can be formed by the loss of hydrogen and C_2H_3 from the parent ion. The peak at 81 m/e in the low-resolution scan may have the structure:

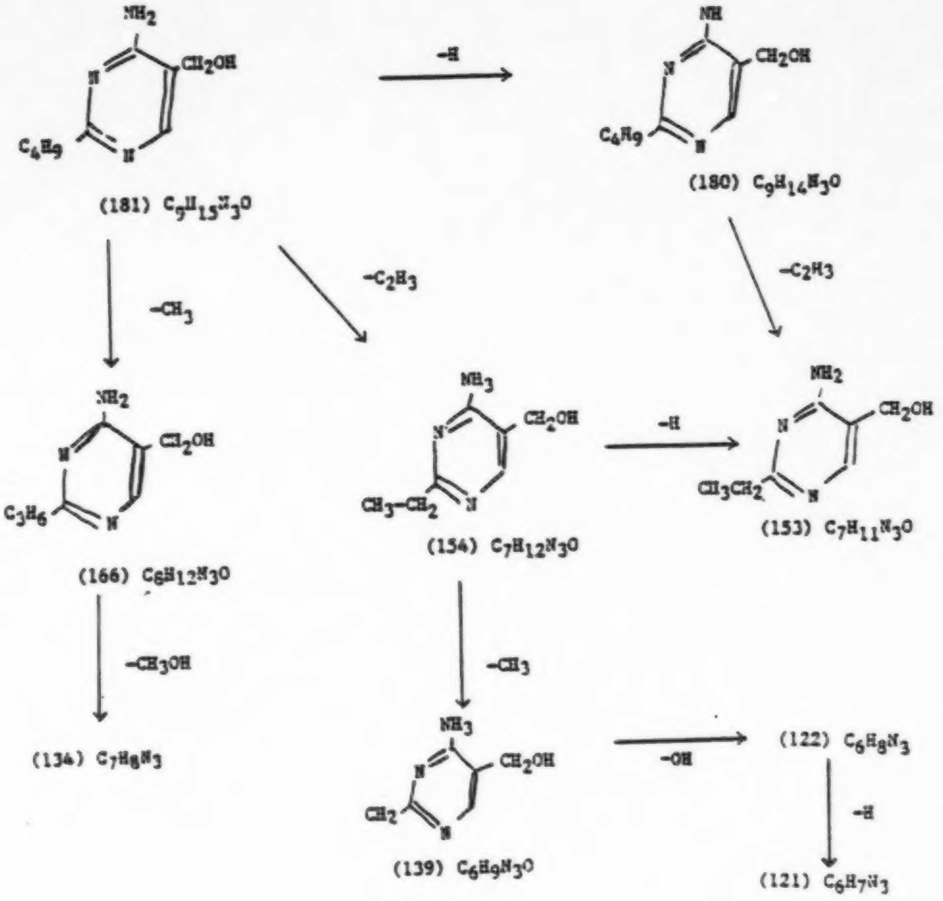


but there was no high-resolution verification of the molecular formula, since the lowest mass scanned was 90 m/e. A proposed fragmentation scheme for the $C_9H_{15}N_3O$ compound is presented on Figure 109. The presence of each

TABLE 43. MASS SPECTRAL PEAK ASSIGNMENTS

Percent of Base Peak	Measured Mass/Charge AMU ± 1 SD*	Assigned Molecular Formula	Theoretical Mass/Charge
34	181.1199 ± 0.0022	$C_9H_{15}N_3O$	181.1216
22	180.1124 ± 0.0007	$C_9H_{14}N_3O$	180.1136
99	166.0961 ± 0.0015	$C_8H_{12}N_3O$	166.0981
34	154.0888 ± 0.0011	$C_7H_{12}N_3O$	154.0981
100	153.0822 ± 0.0019	$C_7H_{11}N_3O$	153.0903
16	139.0748 ± 0.0013	$C_6H_9N_3O$	139.0746
20	134.0711 ± 0.0000	$C_7H_8N_3$	134.0719
64	122.0689 ± 0.0004	$C_6H_8N_3$	122.0719
47	121.0623 ± 0.0002	$C_6H_7N_3$	121.0641
6	108.0572 ± 0.0003	$C_5H_6N_3$	108.0563
6	107.0469 ± 0.0009	$C_5H_5N_3$	107.0484

*AMU = atomic mass unit.
SD = standard deviation.

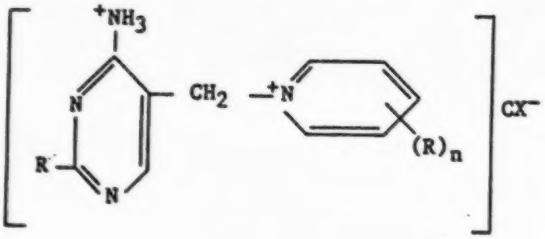

NH2
CH2OH
C4H9
(181) C9H15N3O
-H
NH
CH2OH
C4H9
(180) C9H14N3O
-CH3
-C2H3
-C2H3
NH2
CH2OH
C3H6
(166) C6H12N3O
NH3
CH2OH
CH3-CH2
(154) C7H12N3O
-H
NH2
CH2OH
CH3CH2
(153) C7H11N3O
-CH3OH
(134) C7H8N3
-CH3
NH3
CH2OH
CH2
(139) C6H9N3O
-OH
(122) C6H8N3
-H
(121) C6H7N3

NOTE: All structures have a single positive charge.

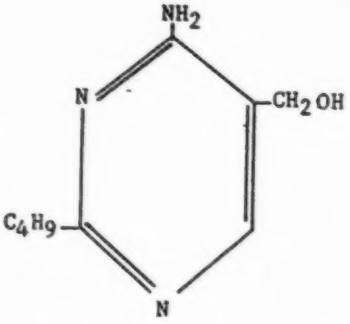
Figure 109. Proposed Fragmentation Scheme.

of the large major ions is accounted for by this scheme; however, this fragmentation scheme should be viewed as only a proposed scheme using common neutral losses to give possible structures for the molecular formulas as derived from the high-resolution mass spectra. The mass spectrum does not indicate if the substitution on the ring is methoxy or carbinol. The lack of a strong M-17 due to a common loss of OH in the mass spectrum contraindicates the carbinol substituent; however, the relatively narrow peak at 3,460 cm^{-1} in the infrared spectrum could be due to the OH stretch of an intramolecular hydrogen bonded OH group. An amino group ortho to a carbinol can form a 6-member intramolecular hydrogen bonded ring with the OH, which would account for the narrow band at 3,460 cm^{-1}; also, the hydrogen bonded ring would help stabilize the OH group with respect to mass spectral fragmentation.

The stereochemistry for the ring substitution pattern was selected based upon the chemical information available on the possible components in the waste stream. One of the products manufactured by this pharmaceutical plant is a quaternary ammonium salt that has the generic structure:



The 2-butyl derivative of these pyridinium salts is manufactured at this plant. The hydrolysis of this pyridinium salt could readily lead to the formation of the proposed structure of Peak 1, 2-butyl-4-amino-5-pyrimidyl-carbinol.



Since a standard was not available for this compound, this structural assignment must be considered tentative. The approximate concentration of this compound was 4 mg/L based upon the integrated area of the base peak at m/e = 153 and a response factor of 1 with respect to anthracene $-D_{10}$.

The peak labeled 1 in Figure 101 was the only compound present in an amount sufficient to obtain an infrared spectrum. The chromatogram also has a group of prominent peaks at retention times of 14 to 15 minutes (several co-eluting components are evident) and a broad peak at approximately 26 minutes; however, the lower concentration of these peaks prevented obtaining infrared spectra. The peak at 26 minutes was a doublet under high-resolution conditions, with highest mass peaks of 204.1159 and 204.1072 with a base peak at m/e of 175. The first peak in the 14 to 15 minute group had a highest mass peak of 141.9254 with a base peak at m/e of 75. The co-elution of the species corresponding to these peaks combined with the lack of infrared data prevented their assignment to particular molecular structures.

A minor peak at a retention time of 14 minutes probably contained glycine co-eluting with other peaks. The mass spectrum of this peak along with the mass spectrum of glycine are presented in Figure 110. Several peaks not attributable to glycine are evident in the mass spectrum; however, the extracted ion current profile shown in Figure 111 indicates that these higher mass peaks are probably due to co-elution.

ORGANICS REMOVAL BY GAC

The GAC pilot plant study was initiated to determine the effectiveness of carbon in removing both SCOD and specific contributors to the SCOD in the effluent. Figures 112 and 113 present gas chromatograph/flame ionization detection (GC/FID) scans of methylene chloride extracts of the influent to and effluent from the GAC pilot plant. These figures illustrate a dramatic reduction of organic components by GAC treatment, especially in the area of the group of unresolved peaks eluting between 15 and 30 minutes in the chromatogram.

Table 44 presents a comparison of the SCOD levels and the total GC/FID areas for GAC influent and effluent samples. SCOD ratios and GC/FID area ratios are also presented. The GC/FID ratios show a higher reduction from GAC treatment than the actual SCOD ratios. This could be due to a higher adsorption of the compounds represented in the GC/FID scan than the total contributors to the SCOD; i.e., the GC/FID scan does not represent the total spectrum of compounds which contribute to the SCOD. The presence of thermally unstable, non-GC stable compounds that contribute to the SCOD but do not pass through the GC would account for the differences in the ratios. The possibility of other non-GC stable compounds is also supported by the fact that the approximate concentration of the highest peak in the GC/MS run (Peak 1) was less than 5 mg/L as compared to a SCOD level in the control pilot plant effluent of several hundred mg/L. Also, it should be noted that on the dates the samples were obtained (11/20 and 12/4), there was significant leakage of SCOD through the column because the GAC study was well beyond the midpoint of the run and a significant amount of the carbon had been exhausted.

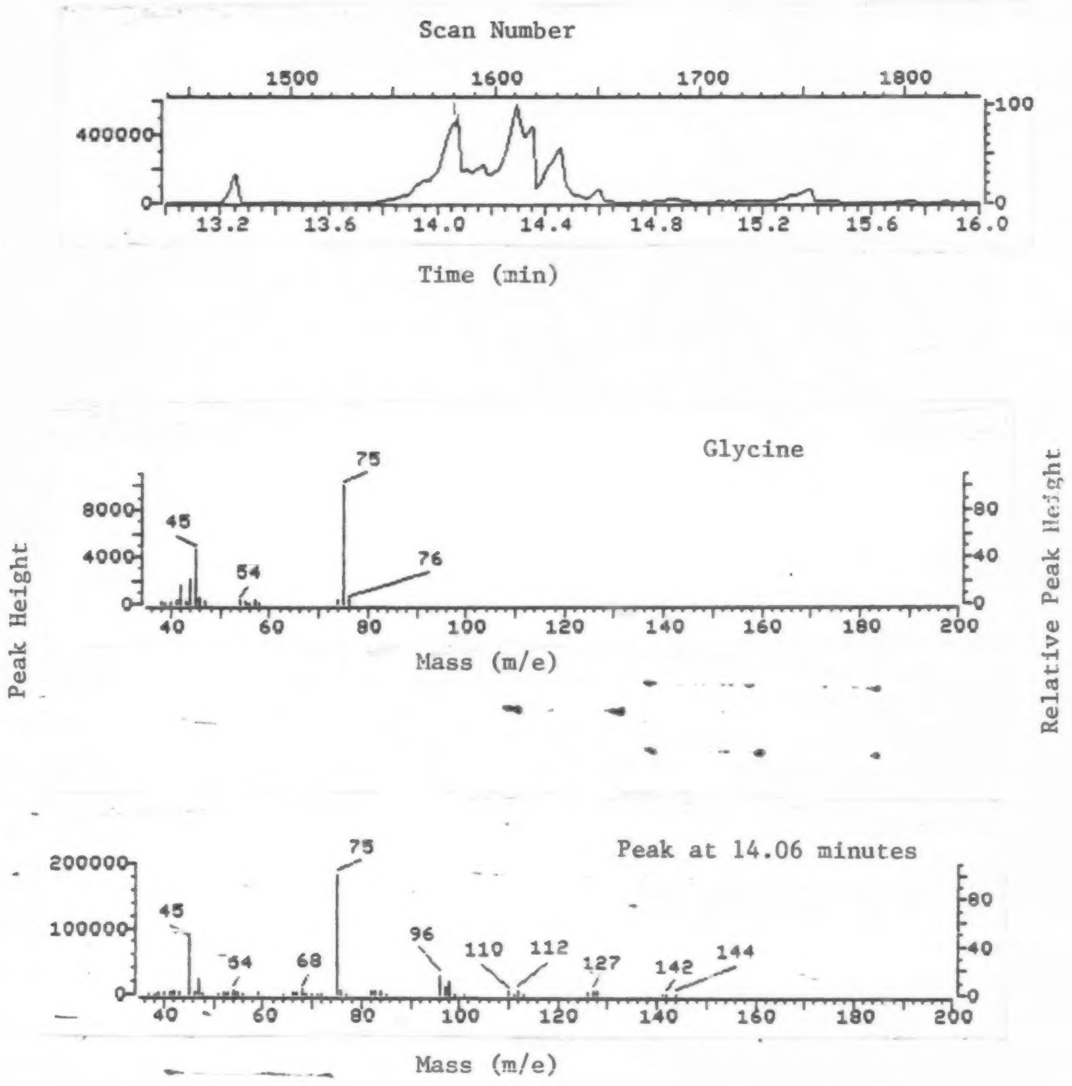


Figure 110. Mass Spectrum of Peak at Retention Time of 14.06 Minutes and Glycine Spectrum.

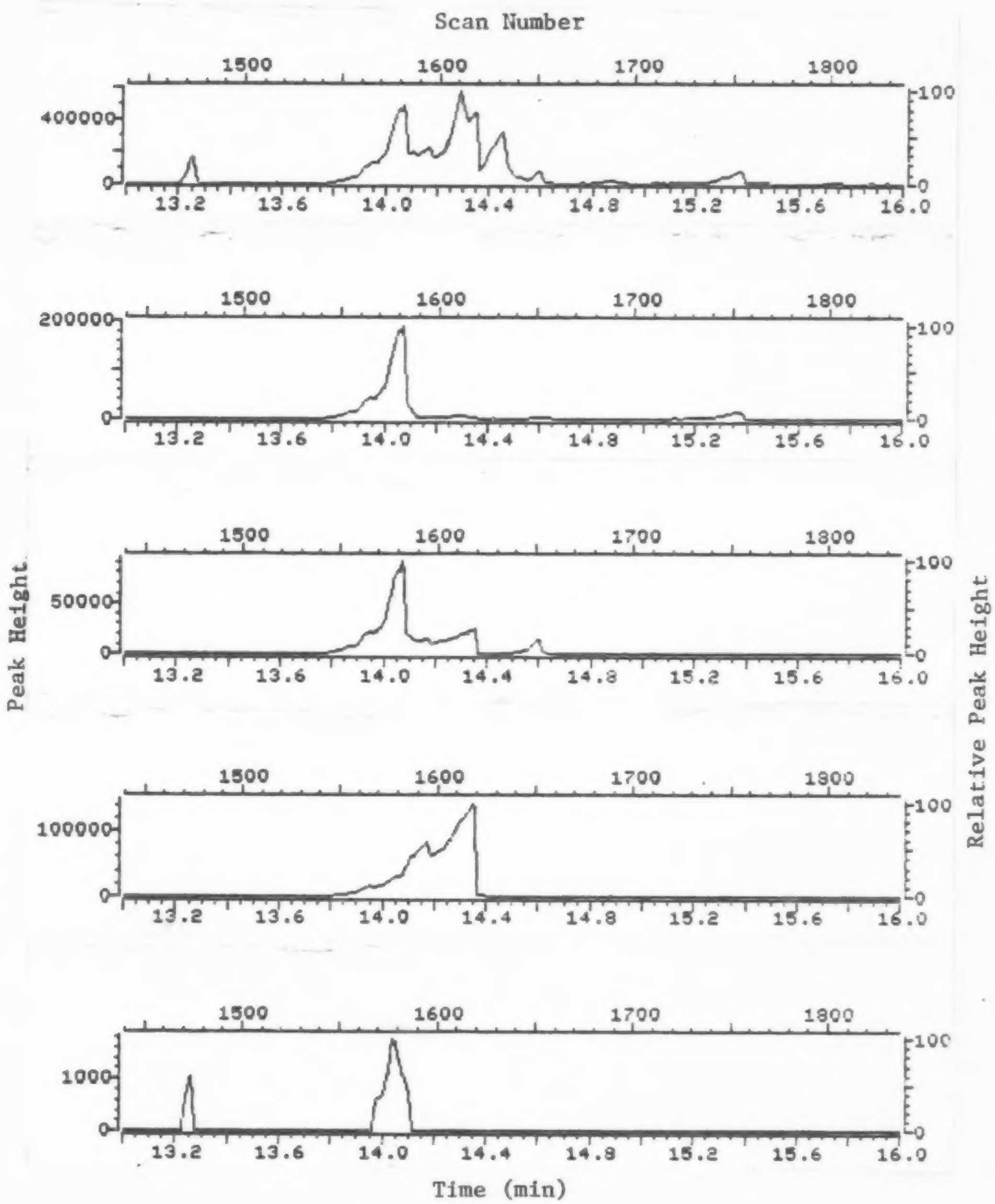
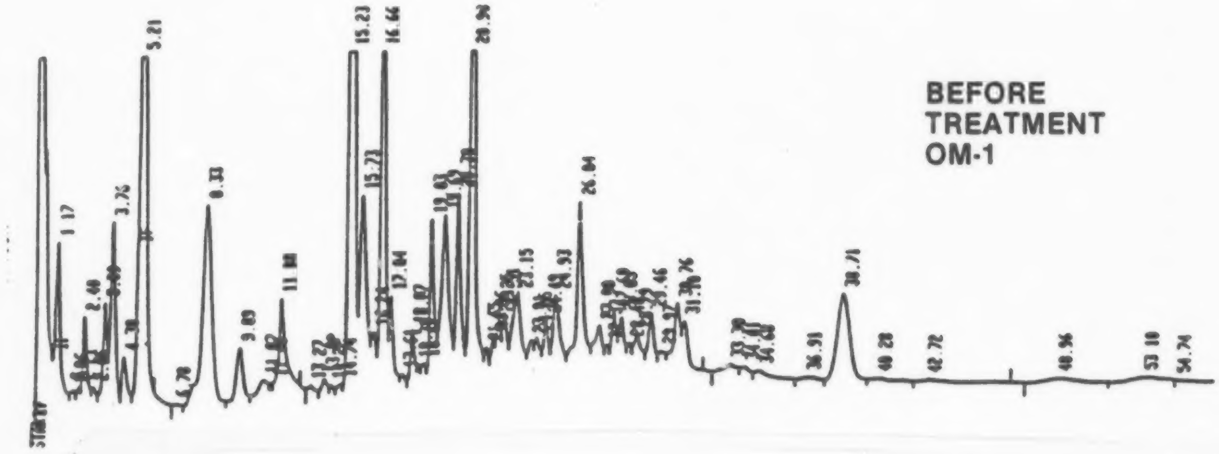


Figure 111. Extracted Ion Current Profile of the Major Ions Near Retention Time of 14 Minutes.



Note: Numbers indicate retention time in minutes.

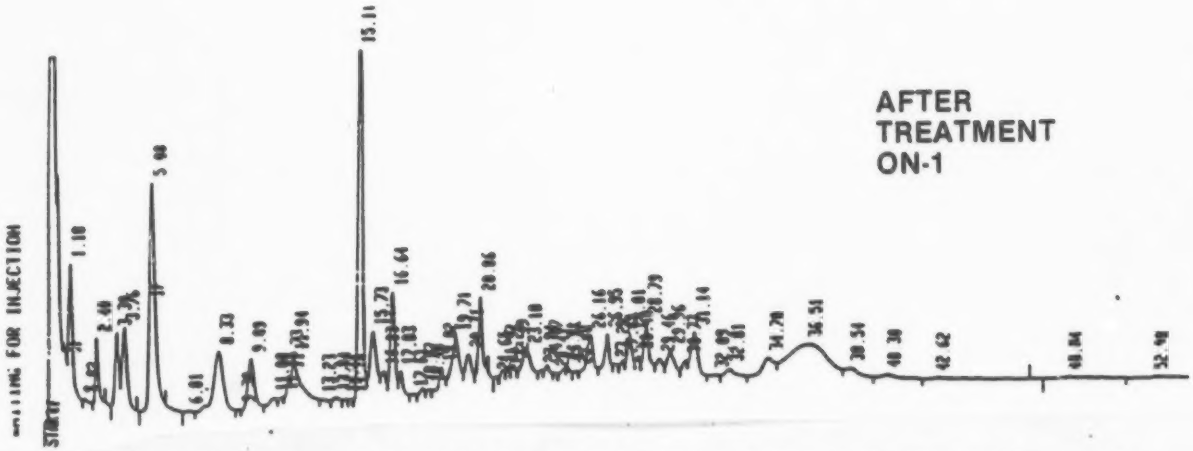
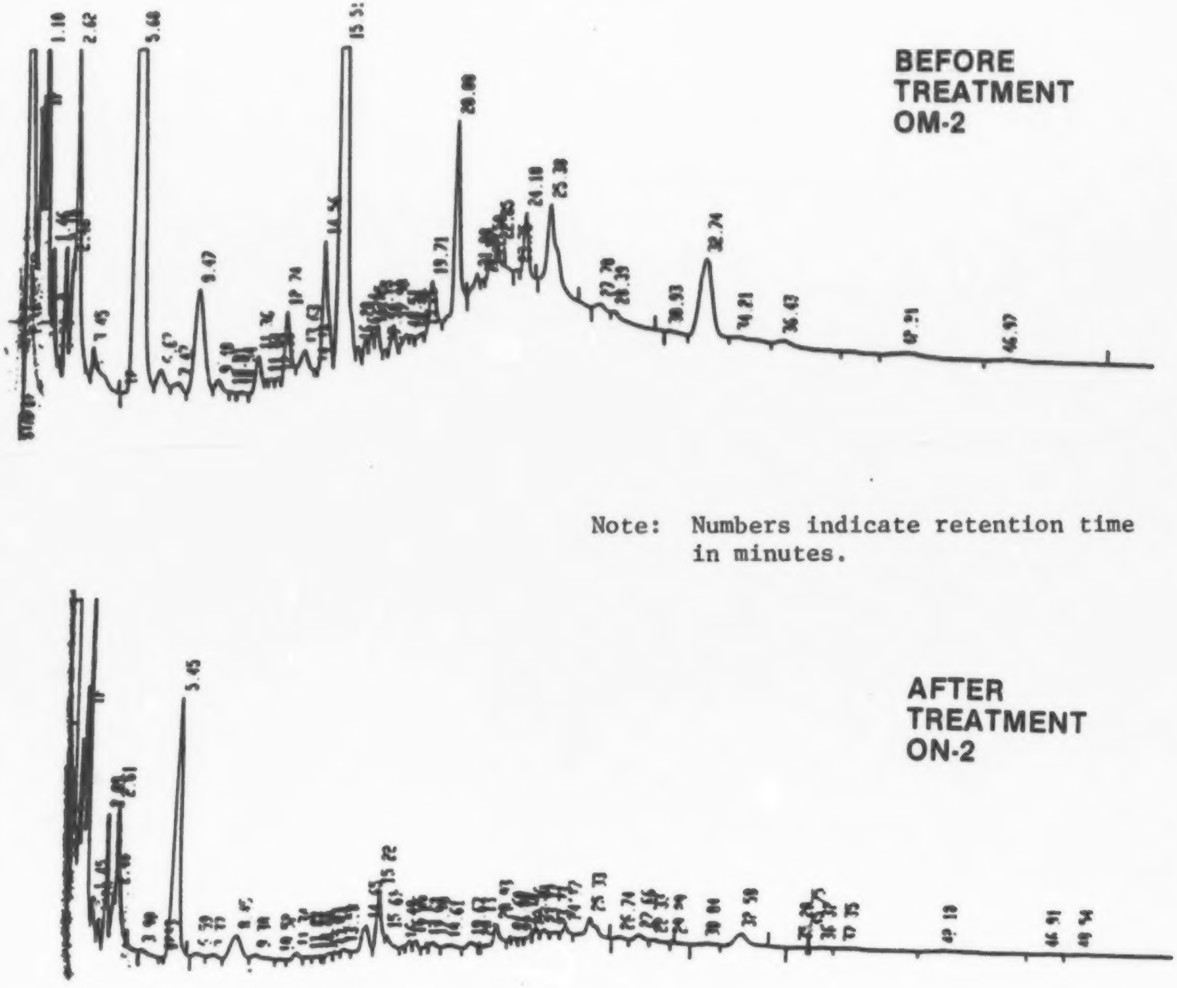


Figure 112. GC/FID Chromatograms of Influent to GAC and Effluent From GAC (Composite sample taken 11/20/84).



Note: Numbers indicate retention time in minutes.

Figure 113. GC/FID Chromatograms of Influent to and Effluent From GAC (Composite sample taken 12/4/84).

SUMMARY

A major component in the gas chromatogram of the pilot plant control biologically treated effluent has been tentatively identified as 2-butyl-4-amino-5-pyrimidyl-carbinol by a combination of high-resolution GC/MS, low-resolution GC/MS, GC/FTIR and chemical information concerning the manufacturing processes at this plant. The concentration of this component was approximately 4 mg/L. Dimethylphenol was also identified as a minor component. The distributions of the GC/MS compounds were similar from samples taken several months apart.

GC/FID scans of samples taken of the GAC influent and effluent treatment reflect the reduction in SCOD observed in the same samples.

TABLE 44. COMPARISON OF SCOD AND GC/FID OF GAC INFLUENT AND EFFLUENT

Sample	SCOD (mg/L)	SCOD (INF) / SCOD (EFF)	GC/FID Total Area	GC Area (INF) / GC AREA (EFF)
OM-1	487	1.95	4.95×10^8	2.8
ON-1	250		1.78×10^8	
OM-2	761	1.53	4.27×10^8	4.4
ON-2	499		9.67×10^7	

NOTE: Above results are from composite samples.

SECTION 11

DISCUSSION

INTRODUCTION

The objective of the research investigation was to optimize treatment for TCOD removal and determine the effluent quality expected from a full-scale plant. The biological and physical-chemical treatment trains evaluated during the pilot study are discussed individually. The study was performed from September to December, 1984.

DISCUSSION OF BIOLOGICAL TREATMENT TESTS

The average TCOD values of the effluent from the full-scale plant and the control pilot plant were 1400 mg/L and 1020 mg/L, respectively, for the entire test period. Based on an average raw waste TCOD concentration of 7060 mg/L for this same period, the TCOD average removals were 80 percent and 85 percent for the full-scale plant and control pilot plant, respectively. These removals exceed the minimum monthly BPT removal of 74 percent. The average SCOD concentration for 50 full-scale plant effluent samples and 81 control pilot plant effluent samples was 829 mg/L and 779 mg/L, respectively.

The addition of PAC to the activated sludge process improved the removal of SCOD. The effect of PAC dosage on SCOD removal is shown in Table 45. The amount of SCOD remaining in the control unit effluent ranged from 8.6 to 10.2 percent of the influent TCOD for the three test periods listed in Table 45. The SCOD remaining in the PAC unit effluent ranged from 5.7 to 2.8 percent of the influent TCOD for PAC dosages ranging from 208 to 1520 mg/L, respectively. At a dosage of 208 mg/L PAC, the PAC pilot unit effluent contained 56 percent of the control unit effluent SCOD for the same period. At dosages of 496, 827, and 1520 mg/L PAC, the PAC pilot unit effluent contained 47, 32 and 33 percent of the control unit effluent SCOD, respectively.

The addition of PAC also slightly improved the settling rate of the mixed liquor. Average oxygen uptake rates for mixed liquor containing PAC were about the same as for the control unit mixed liquor. The cell 1 oxygen uptake rates were higher for the PAC units than for the control unit.

Nitrification developed in all three pilot plant units. The two pilot plants containing PAC also developed denitrification, which caused some floating MLSS in the clarifiers. The units containing PAC later developed a viscous floating layer that was difficult to re-disperse in the mixed liquor. These units contained abundant to excessive amounts of Type 021N and large amounts of *H. hydrossis* filamentous organisms. The control unit, operated under similar conditions, did not develop the viscous layer during the test period. Although *H. hydrossis* was abundant in the control unit, only a few of Type 021N organisms were found. It appears that the presence of PAC may enhance the growth of organisms such as denitrifers and Type 021N that may not be able to flourish in a conventional activated sludge system. The activated sludge system used in these tests--a three cell aeration tank operated at a low F/M ratio - is a configuration often used to promote nitrification. The association of Type 021N with nutrient deficiency also suggests that the development of Type 021N may be controlled in the PAC biological unit by more closely monitoring effluent residuals and nutrients during critical periods.

DISCUSSION OF PHYSICAL-CHEMICAL TREATMENT TESTS

In the physical-chemical pilot study, the full-scale plant biologically treated final effluent was further treated by chemically assisted clarification, multi-media filtration and granular activated carbon. The TCOD concentration of the pilot plant clarified effluent was 977 mg/L for 43 observations as shown in Table 46. This represents a reduction of 31 percent of the full-scale plant effluent TCOD. Multi-media filtration further reduced TCOD by another 100 mg/L.

Table 45. Effect of PAC Dosage on SCOD Removal

Test Period	Day 34-47	Day 62-65	Day 34-47	Day 71-76
PAC Dosage, mg/L	208	496	827	1520
Influent TCOD, mg/L	8120	7420	8120	6810
Control Unit Effluent SCOD, mg/L	825	670	825	583
PAC Unit Effluent SCOD, mg/L	459	314	265	194
SCOD Remaining, % of Feed TCOD				
Control Unit	10.2	9.0	10.2	8.6
PAC Unit	5.7	4.2	3.3	2.8
PAC Unit Effluent SCOD, % of Control Unit Effluent SCOD	56	47	32	33

Table 46 also compares effluent SCOD values. The pharmaceutical plant effluent SCOD averaged 830 mg/L. In comparison, chemical addition (alum dosages ranged from 200 to 1340 mg/L), clarification and filtration effluent SCOD average concentrations were 689 mg/L and 657 mg/L respectively. Thus, it is evident that the pretreatment technologies (clarification and filtration) were about 20 percent efficient in removing the soluble TCOD fraction from the full-scale plant effluent.

Table 46 shows that GAC was capable of treating the pharmaceutical plant effluent to low TCOD and SCOD levels. For GAC Run No. 1, TCOD from the carbon effluent ranged from 144-459 mg/L for 17 observations. Similar results were also obtained for GAC Run No. 2. The range of TCOD in the effluent was from 123-897 mg/L for 42 analyses.

TABLE 46. PHYSICAL-CHEMICAL TECHNOLOGY EFFLUENT TCOD

Treatment Technology	Average TCOD,* mg/L (n)	Average SCOD,* mg/L (n)
Raw Waste	7060 (83)	**
Full-Scale Plant Effluent	1410 (57)	830 (55)
Pilot Plants		
Clarifier Effluent	977 (43)	689 (51)
Filtration Effluent***	877 (70)	657 (69)
Activated Carbon Effluent		
Run No. 1##	275 (17)	199 (18)
Run No. 2###	~~651 (42)~~	251 (42)

*From composite sample results only.
**No data taken.
***Filter performance was not typical of a well designed and operated unit.
#Activated carbon effluent averages are for entire run and not to some specific effluent SCOD concentration.
##For sample collection period 9/11 - 10/12/84.
###For sample collection period 10/24 - 12/4/84.

The primary purpose of the GAC study was to remove SCOD. Thus, the efficiency of GAC can be better illustrated by evaluating this parameter. The range of effluent SCOD for Run No. 1 and No. 2 was from 88-371 mg/L and 64-499 mg/L, respectively.

It must be remembered that the GAC will become exhausted with time and must be replaced periodically to insure that effluent TCOD concentrations will be consistently achieved. The amount of carbon that will be required for a given volume of wastewater has been previously shown on Figure 98.

It may be possible, after operating experience is gained, to reduce carbon usage by either blending carbon effluent with filtered effluent, or increasing the allowable effluent SCOD concentration.

BIOLOGICAL/PHYSICAL-CHEMICAL SCOD EFFLUENT COMPARISON

It should be pointed out that a PAC dosage of 500 mg/L produced an average effluent SCOD from the biological unit of 300 mg/L. In comparison, the GAC effluent maximum SCOD was about 300 mg/L, with the average effluent SCOD being somewhat less than 300 mg/L.

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